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STUDIES ON OXIDATION-REDUCTION.

IV. ELECTRODE POTENTIALS OF INDIGO SULPHONATES, EACH IN EQUILIBRIUM WITH ITS REDUCTION PRODUCT.

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Introduction.

From ancient India, through the trade routes of the world, spread the first knowledge of indigo. The distribution of this commodity was not always accompanied by an appreciation of its best use. Pliny (*cf.* Thorpe and Ingold), for instance, writes of indigo as a *pigment*. But the Indian dyers had early discovered that the substance is transformed to soluble indigo-white in an alkaline fermentation vat;¹ that indigo-white penetrates cloth; and that it is then fixed as the blue, insoluble dye on exposure to air. Thus the principle of vat dyeing was introduced. At various times and places the vat fermentation was replaced, as it is to-day, by inorganic reducing agents. Consequently, when processes of reduction and of oxidation were systematically formulated in the early part of the last century, the reversible transformation $\text{indigo} \rightleftharpoons \text{indigo-white}$ was already in mind to be made familiar as an example of oxidation-reduction. When the biological nature of fermentation was revealed the bacterial formation of indigo-white became one of the first classified instances of biological reduction.

To the reversible system $\text{indigo} \rightleftharpoons \text{indigo-white}$,² investigators have turned again and again as an aid in the study of biological oxidation reduction. When Gunning (1878) brought the culmination of his researches to the attention of the French Academy of Sciences and faced Pasteur with the contention that bacteria can not grow without free oxygen, Pasteur (1878) replied by resting his case upon then recent experiments with indigo. He had frequently shown that bacterial growth may occur in culture media exhausted of oxygen, and now he shows that this oxygen exhaustion is sufficient to prevent coloration of indigo-white. His conception of the extent of deoxy-

¹ The comparatively simple reduction of indigo itself should not be confused with the complex fermentative preparation of indigo from the glucoside of the indigo plant.

² Where there is no occasion to make a distinction we shall let this system represent any one of those to be discussed.

generation attained may be judged by his frequent use, in other papers on this subject, of the adjective "absolute."

A different concept—a concept of degree in oxygen requirement—is the basis of Ehrlich's (1885) work in which he made use of differential reduction of dyes. These investigations of Ehrlich revived that research on bacterial reduction which dates at least from Helmholtz (1843), and led to the study of differential reactions between various bacteria and various dyes. Among the dyes so studied, indigo carmine was employed by Spina (1887), Cahen (1887), Müller (1889), Wolff (1902), and others. An interesting study of the conduct of indigo carmine in anaerobic cultures was made by Kitasato and Weyl (1890).

It is generally conceded that the origin of the well-known methylene blue reduction test of the bacterial quality of milk is found in the opening page of *Le Lait*, where Duclaux (1894) cites the rapid reduction of indigo carmine as evidence of bacterial activity. Vaudin (1897) correlated this test with bacterial numbers. This test is, in principle, identical with the putrescibility test of sewage; and here indigo carmine has again played a part in the development. (H. W. Clark and Adams (1908). Compare Clark and Cohen (1921).)

The conduct of indigo carmine in various tissues has not been very clearly defined. Gautier (1891) observed reduction and considered it evidence of a primary anaerobic phase of metabolism in all living cells. Štolc (1912) claimed that indigo blue remained in the protoplasm of *Pelomyxa* and was eliminated unreduced. Schutzenberger and Risler (1873) claimed that indigo-white, produced by hydrosulphite, takes up more oxygen from blood *in vitro* than can be extracted by the mercury pump. Lambling (1888) verified this and from spectroscopic studies concluded that indigo-white does not reduce oxyhemoglobin further than to hemoglobin. On the other hand, Shafer (1908) maintained that leuco-indigo carmine may circulate as such in the blood of the living rabbit, may be held unoxidized by tissues, and is oxidized after passing into the lumens of the convoluted tubules. He also states that "there is no direct proof that indigo carmine is reduced in the living animal body." Indigo carmine was early used by Heidenhain (1874) in a study of kidney secretion. His observation that the cells of the tubules stain blue, while the capsules of Bowman remain colorless, was considered an impressive argument in favor of Bowman's (1842) theory of secretion; but Nussbaum (1878) suggested that the absence of stain in Bowman's capsule is due either to the high dilution of the passing indigo carmine or to its reduction to the colorless form. Shafer (1908) supports Heidenhain in finding no staining of the capsule by indigo carmine; but with Dreser (1885) he believes that indigo carmine is not reduced in the kidney. Höber and Kempner (1908) placed indigo carmine in the lymph sac

of the frog and studied its excretion. They found the excretion to be chiefly by the second segment of the tubules and that the indigo carmine became apparent only after oxidation with hydrogen peroxide. In commenting on the work of Heidenhain, Nussbaum (1878) cites an experiment showing that the liver may take up and reduce indigo. The absorption was made evident only on oxidizing the reduced indigo, a precaution to be remembered wherever indigo is used as a stain. Indigo carmine (indigo disulphonate), which is now a permissible food color (Pugsley, 1922), has recently been employed by Thomas (1914, 1922) and Thomas and Min Hsu (1922) as a kidney-function test. Hatiegan (1922) used it in a test for hepatic hyperpermeability.

It goes without saying that a substance so well known and so common as indigo should have been employed both with and without reason. A review in the American Journal of Medical Science, 20, 483 (1837), cites the use of indigo as a therapeutic agent in epilepsy, hysteria, amenorrhea, St. Vitus's dance, and infantile convulsions. It has been used by the chemist as a test for urinary sugar, for oxygen, for chlorine, for nitrates, for tannin, and as an indicator for caustic alkali.

Popular writers on the romance of synthetic indigo have emphasized those achievements of the chemist which have led to the artificial production of a pleasing color. But it should be noted that the researches which led to the final synthesis revealed the nucleus of indigo, indole. This group is now found in an essential nutrient, tryptophane, and in an essential hormone, thyroxin. In the metabolism of tryptophane the indole group persists, appearing as indol-ethylamine, a stimulant of smooth muscle, as indole, a bacterial product, and as indican, an end product found in mammalian urine. In plants the occurrence of the indigo-yielding glucoside in the genus *Indigofera* and of free indole in certain odorous flowers is but an indication of the wide distribution of the indole group, a distribution curiously brought to general attention through the discovery that the "royal purple of the ancients," the product of a snail, is brominated indigo. Wherever found, one method of detecting the indole group is to convert it to indigo, and thus the study of the system $\text{indigo} \rightleftharpoons \text{indigo-white}$ is a first, although minor, step toward an understanding of processes of oxidation or reduction by which the indole group in nature is carried through a wide variety of transformations.

In many of the investigations briefly mentioned above, indigo has been used under circumstances or for definite purposes which will hardly bear critical examination. Of these instances we shall later refer to one and shall now mention another, a brief discussion of

which will reveal both the nature and the limitations of our own contribution.

The coloration of indigo-white has been used as a test for free oxygen, and, conversely, the decoloration of indigo blue has been used as an end-point indication of oxygen exhaustion. We have already emphasized, in the first article of this series, the fact that many reversible oxidation-reductions can be accomplished by a variety of reactions and can be formulated by a variety of schemes. We shall show in this paper that whatever the manner in which a given state of the system indigo sulphonate \rightleftharpoons leuco compound is established, that state may be expressed in units of universal applicability in essential accord with the formulations of our second paper. The significance may be illustrated by means of an analogy.

Everyone is familiar with the fact that a certain state of color-change or virage of phenolphthalein indicates only that its aqueous solution has a certain definite hydrion concentration. If now phenolphthalein is to be used as an end-point indicator in the titration of an acid by a base, the acid and base chosen must be such that equivalent quantities mixed in the given concentration furnish a hydrion concentration within the range of color change of phenolphthalein. Otherwise, or if there be present material tending to buffer the solution at or above the zone of hydrion concentration within which phenolphthalein changes color, this indicator will be quite useless for end-point work. The failure to recognize this has led to gross mistakes both in theory and in practice. The first and fundamental task in the development of a rational theory of acidimetric titration was the establishment of the acid-base equilibrium-constant or at least the pH zone of color change of each indicator.

The reader will at once perceive the analogy. Indigo, according to the circumstances of its use, may or may not be valuable as an end-point indicator of free oxygen. Most certainly it has sometimes been employed in solutions poised³ by material active between the true end point of oxygen removal and the potential at which indigo is reduced; but for the present we need not discuss this. We are now concerned in establishing universally applicable data of the oxidation-reduction intensities of different states of the systems. This is a first and fundamental step. Without this information it is easy to misjudge results; and were it worth while, instances of mistakes could be cited from the chemical and medical literature. The establishment of the reduction potentials of each system should make possible the use of that system in the colorimetric estimation of reduction intensity. The possible applications of this fundamental knowledge are numerous.

³ See the first article of this series.

In the previous pages we have used for brevity the expression "indigo \rightleftharpoons indigo-white" where we have intended one or another of the following five systems:

1. Indigo \rightleftharpoons indigo-white.
2. Monosulphonate of indigo \rightleftharpoons monosulphonate of indigo-white.
3. Disulphonate of indigo \rightleftharpoons disulphonate of indigo-white.
4. Trisulphonate of indigo \rightleftharpoons trisulphonate of indigo-white.
5. Tetrasulphonate of indigo \rightleftharpoons tetrasulphonate of indigo-white.

These will be discussed separately, and it will be found that henceforth they must be sharply distinguished.

PREPARATION OF THE SULPHONATES OF INDIGO.⁴

Commercial samples of synthetic and natural (Bengal) indigo which we tested were found to contain impurities as described by Perkins and Bloxam (1907) and Perkins (1907). Purification by sublimation, first used by Crum (1823) was employed by Dumas (1834) in his study of the constitution of indigo and by von Sommaruga (1879) in determining the molecular weight. Bloxam (1905) especially recommends it, but, since we were to depend largely upon recrystallization of the sulphonates, a preliminary purification of indigo was carried out by the possibly less satisfactory method of extraction. The finely powdered, crude indigo was extracted successively with hot ethanol, cold acetic acid, and, again, with hot ethanol, in both of which solvents indigo red and indigo brown are somewhat soluble. The final ethanol extract was no longer reddish, but had a blue tinge. The material was then dried, reground, and washed with ten times its weight of 10 per cent hydrochloric acid solution—first hot and then cold—to extract the so-called indigo gluten and mineral material. It was finally washed with hot water, dried first at 60° C., and finally at 110° C., reground, and bottled. By nitrogen analysis a synthetic indigo was found to have been raised from 94 to 98 per cent purity by this method. By the same criterion, Bloxam's (1905) purest preparation was about 98 per cent indigo. Such was the stock from which most of our sulphonates were prepared.

Bloxam (1906) has detailed the preparation of the sulphonates, and we have followed his descriptions, in the main.

The sulphonates are formed by the action of sulphuric acid. Dependent upon temperature, time of action, and the amount and

⁴ Many authors have distinguished the chief constituent of crude indigo by the term "indigotin" or "indigotine." However, this term has been loosely used or made synonymous with "indigo" by otherwise careful writers. That constituent of crude indigo which is regarded as the important constituent and as a chemical individual has been referred to as indigo from the beginning of chemistry. We shall retain this term.

strength of sulphuric acid, there are formed successively the mono, di-, tri-, and tetra-sulphonic acids. Room temperature and 10 to 20 parts of ordinary sulphuric acid to 1 of indigo are conditions yielding the monosulphonic acid. Warming under the above conditions leads to the disulphonic acid, indigo carmine. Moderate warming with sulphuric acid containing 15 per cent excess sulphur trioxide gives the trisulphonic acid; while the tetra sulphonic acid is obtained at high temperatures and with fuming sulphuric acid containing 20 per cent excess sulphur trioxide.

As the degree of sulphonation increases, the practically insoluble indigo is converted into products of progressively higher solubility. Consequently, in the crystallization of the salts the tendency is for the contaminant to be one or more of the lower sulphonates. The aim in sulphonation should be, therefore, to carry the reaction as completely as possible to the stage desired without oversulphonation.

Potassium indigo monosulphonate was prepared as follows: One part indigo and 20 parts concentrated sulphuric acid were thoroughly mixed and allowed to stand one hour at room temperature. The mixture was frequently stirred and the progress of the reaction tested by transferring a drop of the mixture into water. When a violet solution in hot water was obtained, the whole mass was mixed with enough water to dilute the sulphonic acid approximately ten times. The diluted mixture was allowed to stand several hours and the mono sulphonic acid settled out. The precipitate was filtered with suction on a Büchner funnel and was washed with a little water. The filtrate, which may have contained some disulphonic acid, was discarded.

The reddish precipitate was dissolved in boiling water (approximately 300 cubic centimeters of water for each gram of original indigo used) and filtered. To the hot filtrate, powdered potassium carbonate was added, a little at a time, with stirring, until a precipitate began to occur. Then about 100 cubic centimeters of a 50 per cent solution of potassium acetate were added and the whole was cooled first in water and then in ice to 5°. A precipitate of potassium indigo monosulphonate formed. This salt was not definitely crystalline. It was purified by dissolving in boiling water and precipitating with the addition of a few cubic centimeters of the potassium acetate solution while chilling in ice and salt. This process was repeated. Then followed two crystallizations from water without addition of potassium acetate. Finally the sulphonate was filtered on hardened paper and washed with a little water and with ethanol to remove traces of potassium acetate. The compound was heated in an oven at 60° for two hours and at 80° for one hour, to free it from ethanol. It was then heated at 100° for a short time until it separated from the hardened filter paper.

Two sets of the potassium monosulphonate were made; preparation 1 was on a small preliminary scale; preparation 5 on a large scale. The analyses of the samples are given in Table I.

Since preparation 5 was made from an unpurified synthetic indigo, it was thought possible that it might contain some indigo red monosulphonate. Accordingly it was ground with ethanol in which indigo red sulphonates are soluble. Preparation 5 was slightly soluble in 95 per cent ethanol but with a blue color. After treatment with ethanol the insoluble part was recrystallized from water and labeled 5 A.

TABLE I.—Analyses of indigo sulphonates.

Substance.	Preparation number.	Nitrogen.		Sulphur.		Potassium.		Formula.
		Found.	Calculated.	Found.	Calculated.	Found.	Calculated.	
Potassium indigo monosulphonate.	1	7.25	7.36	—	—	10.17	10.28	$C_{16}H_9N_2O_2(SO_3K)$.
	5	7.31	7.36	8.24	8.43	15.5	15.69	
	2	5.49	5.62	—	—	15.95	15.69	
Potassium indigo disulphonate.	6	5.47	5.62	12.56	12.87	16.14	15.69	$C_{16}H_9N_2O_2(SO_3K)_2$.
	17	5.45	5.62	12.72	12.87	15.78	15.69	
	20	5.69	5.62	12.64	12.87	18.82	19.02	
Potassium indigo trisulphonate.	7	4.60	4.54	14.48	15.69	18.59	19.02	$C_{16}H_7N_2O_2(SO_3K)_3$.
	23	4.49	4.54	15.24	15.60	21.29	21.29	
Potassium indigo tetrasulphonate.	4	3.92	3.81	—	17.45	21.73	21.29	
	8	3.80	3.81	16.82	17.45	20.84	21.29	$C_{16}H_5N_2O_2(SO_3K)_4$.
	18	3.79	3.81	17.15	17.45	—	—	

Potassium indigo disulphonate was prepared as follows: One part indigo and 20 parts concentrated sulphuric acid were heated on a water bath one and one-half to two hours with frequent stirring. The product was poured into water, 200 parts, and the mixture stirred and filtered hot. After cooling to about 15° to allow any monosulphonic acid present to settle out, the solution was filtered again. Practically no insoluble matter was present. The filtered solution was then treated with solid potassium carbonate, a little at a time, with stirring, until the potassium salt of the dye showed evidence of precipitating out. About 100 c. c. of a filtered 50 per cent solution of potassium acetate were then added, and the mixture was brought to boiling and filtered hot. Cooling first in water and then to 5° in ice for an hour gave a precipitate of blue needles, more or less contaminated with potassium sulphate. The precipitate was filtered on a Büchner funnel. If the filtrate happened to be a deep blue, a little of the potassium acetate solution was added and the mixture warmed with stirring and chilled as before until more disulphonate began to crystallize out. This second precipitate was filtered on the same Büchner funnel, washed with potassium acetate to wash out sulphate and with ethanol to wash out the acetate. The precipitate was purified by taking up in a minimum amount of boiling water, filtering hot, cooling in ice, and filtering

the precipitate. This process of solution and precipitation was repeated two or three times. The potassium indigo disulphonate crystallized in bunches of needles. The dry salt is purplish blue.

Preparations numbered 2, 6, and 17 were made by this method. Preparation 2 was a preliminary sample on a small scale; preparation 6 was made on a large scale, using an unpurified synthetic indigo; preparation 17 was made from purified indigo after the methods of making and purifying the compound were well understood, and was the best of the three. The results of analysis are given in Table I.

Preparation No. 20 was made in a somewhat different way from the other disulphonates, so the method is given in detail. This preparation was intended to be a trisulphonate, but by an error the fuming sulphuric acid was added in half the quantity intended, giving about 10 per cent excess sulphur trioxide instead of 15 per cent.

The preparation was made as follows: Sixty grams of the purified synthetic indigo were mixed with 210 grams of concentrated sulphuric acid and 195 grams of sulphuric acid containing 23 per cent excess sulphur trioxide. The stirred mixture was warmed between 40° and 50° for three hours, with the lower temperature predominating, and was then poured slowly into 6,000 c. c. of water. The solution was cooled and filtered from a little insoluble matter. The filtrate was treated with potassium carbonate and then with a 50 per cent solution of potassium acetate until heavy precipitation began. It was then boiled, chilled in ice, and filtered, giving precipitate 1. The filtrate from precipitate 1 was treated with more potassium acetate and the mixture boiled, chilled, filtered, and the precipitate 1—a combined with precipitate 1.

The combined precipitate and paper were placed in 4,000 c. c. of boiling distilled water, stirred and filtered. The filtered solution was then chilled in ice for one hour. Good precipitation occurred, suggestive of the disulphonate in crystalline appearance and in the color of the solution in water. The filtrate from precipitate 2, treated with 50 c. c. of potassium acetate and chilled, gave precipitate 3. Precipitates 2 and 3 were filtered separately and the filtrates discarded. The precipitates 2 and 3 combined were dissolved in 3,000 c. c. of boiling water, cooled, chilled, stirred up with 200 c. c. of 95 per cent ethanol to settle the precipitate and to free it from any potassium acetate that might be present. The filtered precipitate was precipitate 4.

Precipitate 4 was dissolved in 2,000 c. c. of boiling water, cooled, chilled in ice two hours, filtered, and washed with 100 c. c. of 50 per cent ethanol, dried by suction one hour at 60°, ground and bottled as preparation 20. It contained 8.82 per cent moisture, determined by starting the oven at 60° and keeping the sample at 120–122° for

three and one-half hours. On the basis of dry weight, preparation 20 gave the analyses shown in Table I.

Potassium indigo trisulphonate was prepared as follows: Fifty grams of purified indigo were treated with 500 c. c. of sulphuric acid containing 15 per cent excess sulphur trioxide. The mixture on the water bath was kept between 45° and 55° for three and one-half hours, with frequent stirring. The mixture was poured into water, made up to 5,000 c. c., and filtered. The filtrate was partly neutralized with solid potassium carbonate, a little at a time, with stirring, and then treated with a 50 per cent solution of potassium acetate until a heavy precipitate formed in the still acid mixture. The mixture was then brought to boiling to put the precipitate into solution and was filtered hot. The filtrate, cooled in water and then in ice for an hour, gave a heavy precipitate of dye and inorganic potassium salts. The precipitate was filtered off, and the filtrate again chilled. A second precipitate occurred, which was filtered with the first on Büchner funnels.

This material was dissolved in boiling water and the solution filtered from some insoluble material. The crystals obtained by cooling were filtered and dissolved in 2,000 c. c. of boiling water. When chilled, this solution gave precipitate 3. This, after filtration, was dissolved in 1,000 c. c. boiling water. On cooling, the precipitate which formed was stirred with 200 c. c. 90 per cent ethanol to extract acetate. The mixture was filtered on hardened paper and washed with 100 c. c. 90 per cent ethanol. It was partially dried with suction, pressed between several hardened filter papers, dried first at 60° one hour, then at 70°, and finally ground, and bottled. This was preparation 23, which, after drying at 120°, was found to contain 13.11 per cent moisture. The analyses are shown in Table I.

Other preparations of potassium trisulphonate, preparations numbered 3 and 7, were not as satisfactory as number 23. Sample No. 3 was made on a small scale with indigo treated at 50° with sulphuric acid containing 20 per cent excess sulphur trioxide and proved to be largely tetrasulphonate, after the preliminary measurements as of a trisulphonate had been reported (Sullivan and Clark 1921). Sample No. 7 erred on the other side in containing more or less disulphonate.

Potassium indigo tetrasulphonate was prepared as follows: Forty grams of purified indigo were stirred into a paste with 75 grams of concentrated sulphuric acid and 250 grams of sulphuric acid containing 50 per cent excess sulphur trioxide. The mixture was heated at 110° for 40 minutes, with frequent stirring. The mixture was allowed to cool to 50° and was then poured into 5 liters of water. While still warm the purple solution was filtered. The solution was treated with solid potassium carbonate, with stirring, until there was

some evidence of salting out. The salting out was completed by the addition of a 50 per cent solution of potassium acetate. A heavy precipitate occurred. The mixture was then brought just to boiling when the precipitate went into solution. The mixture was next cooled and chilled in ice for one hour. A heavy precipitate occurred, a mixture of the tetrasulphonate and potassium sulphate. The precipitate was collected on a Büchner funnel and was washed with a little potassium acetate. It was dissolved in 2,000 c. c. of hot water. The solution was filtered warm and chilled to 0° in ice and salt. A heavy precipitation of large, transparent, red, crystalline plates occurred. These were filtered and washed with 95 per cent ethanol. The tetrasulphonate was further purified by crystallization from 1,000 c. c. of aqueous solution. The final crystals were filtered on hardened filter paper and washed with a little water. Dried for a time by suction and then at 85° for an hour, the tetrasulphonate was ground and bottled as preparation 18. Dried at 120° it was found to contain 8.14 per cent moisture. With correction for moisture, the compound furnished the analyses shown in Table I.

Three preparations of potassium indigo tetrasulphonate were made. Preparation 4 was made on a small scale and was used up in the measurements described in our preliminary paper (Sullivan & Clark, 1921). Preparation 8 was from unpurified indigo. Preparation 18 is considered our best sample.

ANALYSES OF THE INDIGO SULPHONATES.

Moisture was determined by drying the samples at 120–125°, as recommended by Halland (1918). The samples were started at 60° and were gradually brought to 120–125° and dried to a constant weight. The dried samples were very hygroscopic.

Nitrogen was determined by the Kjeldahl method.

Sulphur was determined as BaSO_4 after fusing with 10–15 parts of a mixture of 7 parts sodium carbonate and 1 part potassium nitrate.

Potassium was determined from the ash as potassium sulphate, and, in a few cases, as potassium platonic chloride.

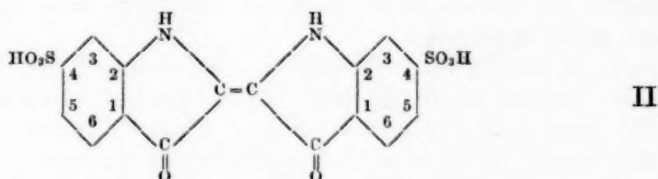
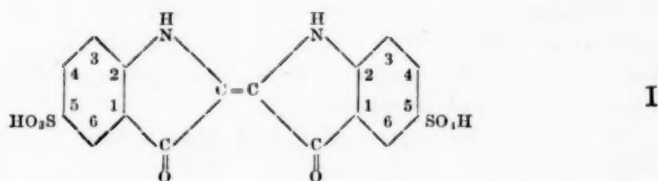
Ashing was done at a final temperature of 780° in an electrically controlled electric furnace. If not white, the ash, treated with a drop of nitric acid and a drop of concentrated sulphuric acid, was placed in the oven again and the temperature raised gradually to 780°. The white ash was presumed to be K_2SO_4 . The potassium determined by precipitation as potassium platonic chloride agreed with the potassium computed from ash as K_2SO_4 . The averages of analyses are given in Table I.

POSITIONS OF SULPHONIC ACID GROUPS.

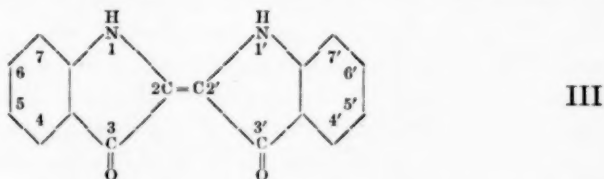
The sulphonates of indigo have long been known, for references in the very early literature are to be found. So far as we have ascertained, the first salts were made by Crum in 1823. He prepared the mono- and the disulphonates. Dumas (1836, 1837) also prepared sulphonates. He called the monosulphonic acid "sulphopurpuric acid," and the disulphonic acid he called "sulphindyllic acid." Apparently Juillard (1892) separated the trisulphonate from a mixture, and later Hönig (1899) gave details for its preparation.

Vorländer and Schubart (1901) and Schubart (1902) synthesized from intermediates in which the position of the sulphonic acid was known, isomeric disulphonates of indigo:

(I) With the sulphonic group para to the NH; (II) with it meta to the NH.



These disulphonates Vorländer and Schubart designated as the 1.2.5 disulphonate and the 1.2.4 disulphonate. The 1.2.5 disulphonate they found to be identical with indigo carmine. On the basis of Baeyer's formula and the now customary atom numbering



(III) we can call Vorländer and Shubart's 1.2.5 disulphonate the 5.5' disulphonate; their 1.2.4 disulphonate the 6.6' disulphonate.

The 5.5' disulphonate, which they found identical with indigo carmine, gives a precipitate with barium chloride and basic lead acetate and is insoluble in excess of these precipitants. The 6.6' acid (Vorländer and Schubart's 1.2.4 acid) gives no precipitate in

dilute solutions with barium chloride, and the precipitate with basic lead acetate is soluble in excess of the precipitant. Spectroscopically, also, the isomers were found to differ.

The potassium disulphonate employed in the present investigation was completely precipitated by barium chloride and with basic lead acetate, so it is probably the 5.5' disulphonate.

Grandmougin (1909, 1921) points out that bromination or sulphonation occurs successively, first in position 5 para to the NH of the indole nucleus, and next in position 7 ortho to the NH.

On the basis of the work of Vorländer, Schubart, and Grandmougin, the positions of the sulphonic groups are as follows: "mono," 5; "di," 5.5'; "tri," 5.5', 7; "tetra" 5.5', 7.7'.

It is possible that some of our preparations may have been mixtures of isomers at the same stage of sulphonation. This could be detected if the characteristic equilibrium potentials of two isomers are distinctly different from one another. Since we have no information on this matter we shall consider the deviations treated in the last section of this paper to be due to contaminations by other sulphonates and not by isomers.

The four sulphonates of indigo have solubilities which increase with the degree of sulphonation. The monosulphonate, while sufficiently soluble in water to give a deep blue solution, precipitates on addition of salts.

With increase in sulphonation, the colors of the dilute solutions shift from an apparently pure blue to a decided reddish blue. Both this shift and a decrease of specific absorption are shown by the absorption curves plotted by Walter C. Holmes (1923) of the Color Laboratory, Bureau of Chemistry, United States Department of Agriculture. Using preparation No. 5 of the "mono," preparation 17 of the "di," preparation 7 of the "tri," and preparation 18 of the "tetra," Holmes (1923) found that, in alcoholic or aqueous solution, sulphonation shifts the absorption band toward the blue, the maximum in ethanol changing from λ 6150 for the monosulphonate to λ 5980 for the tetrasulphonate, and in aqueous solution from λ 6080 for the mono to λ 5900 for the tetrasulphonate. At the same time in either solvent there is developed a greater general absorption in the blue. In alcoholic solution the maxima of the absorption bands are reduced from extinction coefficients 1.63 of the monosulphonate to 0.81 of the "tetra," and the "di" and "tri" lie almost equally spaced between these values. The corresponding data for aqueous solution are not so definite because of the colloidal nature of the monosulphonate. However, the general order is the same.

Dr. Edgar T. Wherry has given us the following descriptions of the crystalline potassium sulphonates:

"*Tetra.*"—Rods and plates with strong pleochroism from brown crosswise to intense blue lengthwise. One refractive index crosswise about 1.50, others indeterminate.

"*Tri.*"—Needles with strong pleochroism from pinkish gray lengthwise to deep blue crosswise. Refractive indices indeterminate.

"*Di.*"—Very minute needles, with some pleochroism from deeper to paler blue. Refractive indices indeterminate.

"*Mono.*"—Very minute needles or plates, with some pleochroism from deeper to paler violet. Refractive indices indeterminate.

Procedure in Electrode Measurements.

The potential measurements were made with the equipment described in the preceding paper of this series; and, in general, the determination of the characteristics of each set of equilibria followed essentially the course of the study of 1-naphthol-2-sulphonic acid indophenol.

In the latter part of the work the troublesome penetration of oxygen through the rubber tube connected to the apparatus shown in Figure 3 of the previous paper was obviated by attaching the apparatus directly to a copper tube leading from the nitrogen purification chain. After being filled, the apparatus was closed, detached for moving, and gas to compensate for removal of solution was furnished by an attached reservoir of nitrogen stored over mercury.

The study of each set of equilibria included three main series of measurements.

(1) First, one or more titration experiments were made in which the oxidant was reduced or the reductant was oxidized at approximately constant pH. This furnished the value of n , the number of electrons concerned in the process. Since n is evidently 2 in all the cases to be cited, we shall not pause to tabulate calculations. The titration experiments also furnish values of the potentials of known mixtures of oxidant and reductant at constant pH in so far as the pH can be controlled or estimated under the circumstances. This control is not always so rigid as in other series of measurements, but in the titrations with ferricyanide we have applied a correction estimated as follows:

The dye solution was prepared by adding 5 c. c. of approximately 0.006 molar leuco-indigo sulphonate to 50 c. c. buffer No. 7. The oxidizing reagent was prepared by making buffer No. 7 approximately 0.004 molar with respect to K_3FeCy_6 and diluting 50 c. c. of this to 55 c. c. It was now assumed that the pH of the buffer was such as to suppress the acid property of the leuco-compound and that the shift in pH which would be produced during the titration would be due to the formation of HK_3FeCy_6 from K_3FeCy_6 and to the altering salt content of the mixture. Therefore an estimate of this effect was made by titrating 50 c. c. buffer No. 7 + 5 c. c. water with buffer

No. 7 + 5 c. c. 0.04 NH_2SO_4 + 0.0522 gm. K_2SO_4 . There is probably a slight overcorrection, due to the fact that HK_3FeCy_6 is not so completely ionized as H_2SO_4 at the pH of buffer No. 7.

While this procedure still leaves a small degree of uncertainty, it is probable that the correction is of the proper order and that the experimental curve, when corrected, will show only slight deviations from the theoretical type when the compound is pure. If, however, the dye under investigation is a mixture of compounds, each capable of a reversible oxidation-reduction, the deviation of the experimental titration curve from the type should be large. This sort of analysis will be discussed later.

(2) The second series of experiments consisted in the measurement of the electrode potentials of known mixtures of oxidant and reductant in solutions the pH values of which were considered identical with those of the buffer diluted to the same concentration as the buffer-dye mixture. These measurements give the potentials of known mixtures at a few pH values.

In these first two series of measurements, pH is assumed to be constant. As shown in previous papers, the electrode equation for this condition is:

$$E_h = E'_o - \frac{RT}{2F} \ln \frac{[S_r]}{[S_o]} \quad (1)$$

(3) The third series of experiments consisted in adding an indefinite, but approximately equimolecular, mixture of oxidant and reductant to different buffer solutions and thus determining the effect of pH change. With this set of data the character of the third term of the equation can be determined (*cf.* the second paper).

Since many of the buffer solutions had the same composition we may save space by tabulating below (Table II) the composition of those most frequently used. Since slight differences of pH occur by reason of variation in stock material and air contamination, no pH values are included in Table II. The pH values given in subsequent tables were determined in each case on the solution used and within a reasonable period before or after its use.

Just as in the study of 1-naphthol-2-sulphonic acid indophenol (see previous paper), so in the study of the indigo sulphonates by the method of mixture, slight but distinct drifts of potential occurred after adding the mixtures to buffer solutions. As in the former case, so in this the values taken, unless otherwise stated, were those of a period of apparent constancy when the curve of drift with time had reached a "plateau." The magnitude of the drift was about the same as that described for 1-naphthol-2-sulphonic acid indophenol, and to the discussion given in the previous paper we have now nothing to add.

TABLE II.—Composition of buffer solutions.

No.	Composition.
1	250 c.c. M/5 KCl + 250 c.c. M/5 HCl + 0 c.c. water.
2	250 c.c. M/5 KCl + 125 c.c. M/5 HCl + 125 c.c. water.
3	250 c.c. M/5 KCl + 30 c.c. M/5 HCl + 220 c.c. water.
5	250 c.c. M/5 KH phthalate + 250 c.c. M/5 KCl + 130 c.c. M/5 HCl + 370 c.c. water.
6	250 c.c. M/5 KH phthalate + 250 c.c. M/5 KCl + 50 c.c. M/5 HCl + 450 c.c. water.
7	250 c.c. M/5 KH phthalate + 250 c.c. M/5 KCl + 500 c.c. water.
8	250 c.c. M/5 KH phthalate + 60 c.c. M/5 KOH + 190 c.c. M/5 KCl + 500 c.c. water.
9	250 c.c. M/5 KH phthalate + 150 c.c. M/5 KOH + 100 c.c. M/5 KCl + 500 c.c. water.
10	250 c.c. M/5 KH phthalate + 215 c.c. M/5 KOH + 35 c.c. M/5 KCl + 500 c.c. water.
11	250 c.c. M/5 KH phthalate + 225 c.c. M/5 KOH + 25 c.c. M/5 KCl + 500 c.c. water.
12	250 c.c. M/5 KH_2PO_4 + 20 c.c. M/5 KOH + 230 c.c. M/5 KCl + 500 c.c. water.
13	250 c.c. M/5 KH_2PO_4 + 60 c.c. M/5 KOH + 190 c.c. M/5 KCl + 500 c.c. water.
14	250 c.c. M/5 KH_2PO_4 + 150 c.c. M/5 KOH + 100 c.c. M/5 KCl + 500 c.c. water.
15	250 c.c. M/5 KH_2PO_4 + 210 c.c. M/5 KOH + 40 c.c. M/5 KCl + 500 c.c. water.
16	250 c.c. M/5 KH_2PO_4 + 235 c.c. M/5 KOH + 15 c.c. M/5 KCl + 500 c.c. water.
18	125 c.c. M/5 H_3BO_3 + 5 c.c. M/5 KOH + 120 c.c. M/5 KCl + 250 c.c. water.
19	125 c.c. M/5 H_3BO_3 + 8 c.c. M/5 KOH + 117 c.c. M/5 KCl + 250 c.c. water.
20	125 c.c. M/5 H_3BO_3 + 15 c.c. M/5 KOH + 110 c.c. M/5 KCl + 250 c.c. water.
21	125 c.c. M/5 H_3BO_3 + 40 c.c. M/5 KOH + 85 c.c. M/5 KCl + 250 c.c. water.
22	125 c.c. M/5 H_3BO_3 + 80 c.c. M/5 KOH + 45 c.c. M/5 KCl + 250 c.c. water.
23	125 c.c. M/5 H_3BO_3 + 120 c.c. M/5 KOH + 5 c.c. M/5 KCl + 250 c.c. water.
25	125 c.c. M/5 KOH + 120 c.c. M/5 KH_2PO_4 + 5 c.c. M/5 KCl + 250 c.c. water.
26	125 c.c. M/5 KOH + 100 c.c. M/5 KH_2PO_4 + 25 c.c. M/5 KCl + 250 c.c. water.
27	125 c.c. M/5 KOH + 60 c.c. M/5 KH_2PO_4 + 65 c.c. M/5 KCl + 250 c.c. water.
28	125 c.c. M/5 KOH + 0 c.c. M/5 KH_2PO_4 + 125 c.c. M/5 KCl + 250 c.c. water.
29	125 c.c. M/5 KOH diluted to 500 c.c. with water.
30	125 c.c. M/5 KOH diluted to 250 c.c. with water.

All measurements were made at $30^\circ \pm 0.02$. All potential differences recorded in this paper are converted to the normal hydrogen electrode standard on the assumption that the hydrogen electrode potential difference in M/20 KH phthalate is -0.2386 . Hydrogen electrode measurements are designated by π_h . Observed reduction electrode potentials converted to the hydrogen standard are designated by E_h . The E_h value of a system of equal parts of total oxidant and of total reductant at constant pH is E'_o . E'_o at pH=0 is designated by E_o , which, with the qualifications stated in our second paper, is the hypothetical normal potential of the system.

ELECTRODE MEASUREMENTS OF THE TETRASULPHONATE.

In Table III are given the results of a titration of reduced, buffered, indigo tetrasulphonate solution with dilute aqueous chromate solution.

TABLE III.—*Titration with chromate of 10 c. c. reduced 0.006 M indigo tetrasulphonate (No. 18) solution in 50 c. c. phthalate buffer No. 5. pH=2.817. Temp. 30°.*

Chromate.	Oxidation.	$\frac{RT}{nF} \ln \frac{[S_r]}{[S_o]}$	E_h	E'_o	Deviation.
c. c.	Per cent.				
0	0	+0.124
2	13.51	+0.0243	+0.1667	+0.1910	+0.0003
5	33.78	+0.0088	+0.1818	.1506	-0.0001
7	47.30	+0.0014	+0.1893	.1907	0.0000
8	54.06	-0.0021	+0.1927	.1903	-0.0001
9	60.81	-0.0057	+0.1934	.1907	0.0000
10	67.57	-0.0093	+0.2092	.1906	-0.0001
12	81.08	-0.0190	+0.2109	.1910	+0.0003
13	87.84	-0.0258	+0.2171	(.1913)	+0.0006
14.8	100.00	+0.320

Average $E'_o = +0.1907$

In Table III, n in the expression $\frac{RT}{nF}$ is assumed to be 2, and $\frac{RT}{nF} \ln$ is then 0.03006 log. E_h is the observed electrode potential difference reduced to the hydrogen electrode standard of reference. From the values of E_h and of $\frac{RT}{nF} \ln \frac{[S_r]}{[S_o]}$ are calculated the values of E'_o by means of the equation

$$E'_o = E_h + \frac{RT}{nF} \ln \frac{[S_r]}{[S_o]}$$

The average value of E'_o is +0.1907, and the deviations from this are given in the last column. These deviations are such as to indicate a fairly pure compound, the titration curve of which conforms closely to the ideal; but they are perhaps smaller than would be found if proper corrections were made for changes in pH during the course of the titration.

As already mentioned, corrections of potential for change in pH during titration were made in experiments with ferricyanide titration. An example of the consequences is shown in Table IV. A similar titration of sample 8 of the tetrasulphonate gave almost identical results. The data of Table IV are charted in Figure 2.

In Table V are given the results of a titration of the oxidant with a titanous solution. In this case the values of E'_o are not so consistent; but the titanium solution is difficult to adjust to known pH and is not stable.

TABLE IV.—*Reduced indigo tetrasulphonate (No. 18) titrated with K_3FeCy_6 . Five c. c. of approximately 0.006 M dye added to 50 c. c. buffer No. 7.*

[pH of 50+5 dilution=3.938.]

K_3FeCy_6 .	Oxidation.	$RT \ln \frac{[S_r]}{[S_o]}$	E_h	E'_o	Acid correction.	E'_o corrected.	Deviation.
c. c.	Per cent.						
0.5	3.45	+0.0436	+0.0870	+0.1306	-0.0601	(+0.1305)
1	6.90	.0340	.0956	.1295	-0.0603	.1293	+0.0007
1.5	10.34	.0282	.1013	.1295	-0.0604	.1291	.0005
2	13.79	.0239	.1056	.1295	-0.0605	.1290	.0004
2.5	17.24	.0205	.1092	.1297	-0.0607	.1290	.0004
3	20.69	.0175	.1122	.1297	-0.0608	.1289	.0003
3.5	24.14	.0149	.1149	.1298	-0.0609	.1289	.0003
4	27.59	.0126	.1173	.1299	-0.0610	.1289	.0003
5	34.48	.0084	.1218	.1302	-0.0613	.1289	.0003
6	41.38	+0.0045	.1257	.1302	-0.0616	.1285	.0000
7	48.27	+0.0009	.1295	.1304	-0.0618	.1286	.0000
8	55.17	-0.0027	.1333	.1309	-0.0621	.1285	-0.0001
9	62.06	-0.0064	.1371	.1307	-0.0623	.1284	-0.0002
10	68.96	-0.0104	.1413	.1309	-0.0626	.1283	-0.0003
11	75.86	-0.0150	.1458	.1308	-0.0629	.1279	-0.0007
12	82.76	-0.0205	.1513	.1308	-0.0631	.1277	-0.0009
13	89.66	-0.0282	.1590	.1308	-0.0634	.1274	-0.0012
14	95.55	-0.0436	.1726	.1290	-0.0636	(.1263)
14.5	100.00						

Average E'_o =0.1286 π_h =-0.2349 E_o =0.3335TABLE V.—*Indigo tetrasulphonate (No. 8) titrated with Ti^{+++} solution. Both solution buffered at pH 6.96.*

Ti^{+++}	Reduction.	$RT \ln \frac{[S_r]}{[S_o]}$	E_h	E'_o
c. c.	Per cent.			
0	0	+0.167
1.00	9.30	-0.0297	-0.0183	(-0.0490)
2.06	19.16	-0.0188	-0.0265	(-0.0453)
3.11	28.93	-0.0117	-0.0317	-0.0434
4.11	38.23	-0.0063	-0.0367	-0.0430
5.11	47.53	-0.0013	-0.0412	-0.0425
6.11	56.82	+0.0036	-0.0459	-0.0423
7.00	65.11	+0.0081	-0.0502	-0.0421
8.00	74.42	+0.0139	-0.0566	-0.0427
8.50	79.06	+0.0173	-0.0608	-0.0435
10.45	97.21	+0.0464	-0.0976	(-0.0512)
10.75	100.00		

Average E'_o =-0.0428

TABLE VI.—*Electrode potentials of mixtures of indigo tetrasulphonate (No. 18) and the reduction product, each added in 0.006 M solution to 50 c. c. buffer.*

Buffer No.	pH	Reductant.	Oxidant.	E_h	E'_o	π_h	$E'_o - \pi_h$	$E'_o - \pi_h$ (averages).
1.....	1.124	c. c. 7 5 5 3	c. c. 3 5 5 7	0.2874 .2984 .2985 .3095	0.2985 .2984 .2985 .2984	—0.0676	0.3661 .3660 .3661 .3660	0.3660
2.....	1.419	7 5	3 5	0.2694 .2797	0.2805 .2797	—0.0853	0.3658 .3650	0.3654
5.....	2.811	5 3	5 7	0.1921 .2032	0.1921 .1921	—0.1689	0.3610 .3610	
5(all solutions new 1 month later).....	2.816	5 5	5 10	0.1914 .2005	0.1914 .1914	—0.1693	0.3607 .3607	
6.....	3.370	5	5	0.1608	0.1608	—0.2025	0.3633	0.3633

Average = 0.3649

What is considered to be a better-controlled method for estimating E'_o (the electrode potential of an equimolecular mixture of oxidant and reductant at constant pH) consists in adding oxidant and reductant in known proportions to a well-buffered solution, as described in the previous paper. In Table VI are given the results of a series of measurements with these solutions added, in the proportions indicated, to 50 c. c. of the buffer solutions. From the ratio of reductant to oxidant and the observed potential difference, E_h , there is calculated the E'_o value for each case. π_h is the hydrogen electrode potential of 50 c. c. buffer + 10 c. c. water. Assuming that this is the hypothetical hydrogen electrode potential of the dye-buffer mixture, we should expect, within the region of pH included, a constant difference $E'_o - \pi_h$. Comment on the variation will be deferred to a later section of this paper.

Table VI shows the variation of E'_o with pH by means of only five instances. These serve to orient the system and the chart relating E'_o to pH may now be completed by using an approximately known mixture and carrying it through a wider range of pH.

TABLE VII.—*Electrode potentials of a mixture of indigo tetrasulphonate (No. 18) and its reduction product, at different pH values of the solution.*

[10 c. c. 0.006 M mixture+50 c. c. buffer.]

Buffer No	pH	π_h	E_h	E'_o	E'_o calculated.	Deviation
1.....	1.138	-0.0684	+0.3010	+0.2976	+0.2966	+0.0010
3.....	2.045	-0.1229	+0.2461	+0.2427	+0.2420	+0.0007
5.....	2.817	-0.1693	+0.1946	+0.1912	+0.1956	-0.0044
7.....	3.928	-0.2361	+0.1326	+0.1292	+0.1288	+0.0004
9.....	5.197	-0.3124	+0.0562	+0.0528	+0.0528	0.0000
13.....	6.268	-0.3767	-0.0068	-0.0102	-0.0094	-0.0008
14.....	6.975	-0.4192	-0.0412	-0.0446	-0.0450	+0.0004
15.....	7.519	-0.4519	-0.0640	-0.0674	-0.0668	-0.0006
20.....	8.081	-0.4856	-0.0751	-0.0785	-0.0859	+0.0074
22.....	9.295	-0.5586	-0.1185	-0.1219	-0.1230	+0.0011
25.....	9.936	-0.5972	-0.1350	-0.1384	-0.1418	+0.0034
26.....	10.975	-0.6596	-0.1710	-0.1744	-0.1735	-0.0009
27.....	11.634	-0.6993	-0.1985	-0.2019	-0.1933	-0.0086

In Table VII are shown the data for a mixture which proved to be 43.5 per cent reductant and 56.5 per cent oxidant. This fixed mixture was added in 10 c. c. quantities to 50 c. c. of buffer solution in each case. The pH and π_h values given are those of the buffer solution+10 c. c. water. The E_h values observed are corrected to the corresponding E'_o values as follows: It is assumed that $E'_o - \pi_h$ for solution 1 is 0.3660, by Table VI. Consequently, in Table VII E'_o in the case of solution 1 is 0.2976. In this same case E_h is +0.3010. The difference, -0.0034, indicating that the mixture was 43.5 per cent reduced, was applied to E_h in all the other cases to give the values of E'_o .

In Figure 3, curve 4 shows the relation of E'_o to pH.

The smooth curve drawn through or near the plotted values was determined by means of an equation to be developed in a later section. The discrepancies between observed and calculated values will be discussed later.

ELECTRODE MEASUREMENTS OF THE TRISULPHONATE.

The first sample of what was supposed, from the method of preparation described in the literature, to be a trisulphonate, was found by titanium reduction to have the same properties as the tetrasulphonate and was so stated in our preliminary report (Sullivan and Clark, 1921). At that time the analyses were not complete. Further study indicated a mixture the effect of which, combined with the error of the titanium method, misled us. Accordingly, new preparations were made.

Preparation No. 23 gave the following results:

In Table VIII are given the results of a titration of the reduced solution with ferricyanide. The E_h values corrected for acidity-change are plotted against pH in Figure 2.

In Table IX are the results of a titration of the reduced solution with chromate.

In Table X are the results of applying the method of mixtures.

In Table XI are the E_h values obtained with a fixed mixture of reductant and oxidant, 10 c. c. portions of which were added to 50 c. c. buffer. The observed E_h values are transposed to the corresponding E'_o values by means of the data of Table X. The resulting E'_o values in Table XI are plotted against pH in curve 3, Figure 3.

In Table X the second series of measurements in solution 2 and the measurements in solution 9 were made with a second solution of the dye. Measurements made in solution 5 (not shown in Table X) gave E'_o values of 0.1578 and 0.1582—average, 0.1580. Since $\pi_h = -0.1689$, $E'_o - \pi_h = 0.3269$, a distinct displacement again as noted in the case of solution 5 with tetrasulphonate (Table VI).

TABLE VIII.—Reduced indigo trisulphonate (No. 23) titrated with ferricyanide. 5 c. c. of approximately 0.006 M dye added to 50 c. c. buffer No. 7.

[pH of 50+5 dilution=3.908.]

K_2FeCy_6	Oxidation.	RT 2F $\ln \frac{[S_1]}{[S_0]}$	E_h	E'_o	Acid correction.	E'_o corrected.	Deviation.
c. c.	Per cent.						
0.5	3.60	+0.0429	+0.0503	+0.0935	-0.0001	(+0.0934)	-0.0019
1.0	7.19	.0334	.0507	.0941	-0.0003	(.0938)	-0.0015
1.5	10.79	.0275	.0366	.0942	-0.0004	(.0938)	-0.0015
2.0	14.39	.0233	.0715	.0948	-0.0005	(.0943)	-0.0010
3.0	21.58	.0169	.0785	.0954	-0.0008	(.0946)	-0.0007
4	28.78	.0118	.0843	.0961	-0.0010	.0951	-0.0002
5	35.97	.0075	.0889	.0964	-0.0013	.0951	-0.0002
6	43.17	+0.0036	.0932	.0968	-0.0015	.0953	.0000
7	50.36	-0.0002	.0974	.0972	-0.0018	.0954	+0.0001
8	57.56	-0.0040	.1015	.0975	-0.0020	.0955	+0.0002
9	64.75	-0.0079	.1055	.0973	-0.0023	.0953	+0.0000
10	71.94	-0.0123	.1101	.0978	-0.0026	.0952	-0.0001
11	79.14	-0.0174	.1156	.0982	-0.0028	.0954	+0.0001
12	86.33	-0.0241	.1224	.0983	-0.0031	.0952	-0.0001
12.5	89.93	-0.0285	.1269	.0983	-0.0332	.0951	-0.0002
13	93.53	-0.0349	.1334	.0985	-0.0034	.0951	-0.0002
13.5	97.12	-0.0460	.1451	.0991	-0.0035	.0956	+0.0003
13.9	100.00						

Average $E'_o = +0.0953$

$\pi_h = -0.2349$

$E_o = 0.3302$

TABLE IX.—Reduced indigo tri sulphonate (No. 23) titrated with chromate.

[5 c. c. 0.005 M dye in 50 c. c. buffer No. 2. pH of 50 c. c. (No. 2)+10 c. c. $H_2O = 1.42$. No correction for pH change.]

Chromate.	Reduction.	RT 2F $\ln \frac{[S_1]}{[S_0]}$	E_h	E'_o	Deviation.
C. c.	Per cent.				
0	0		+0.180		
1	7.09	+0.0336	.2115	+0.2451	+0.0016
2	14.18	+0.0235	.0.2213	.0.2448	+0.0013
3	21.28	+0.0171	.0.2271	.0.2442	+0.0007
5	35.46	+0.0078	.0.2359	.0.2437	+0.0002
6	42.55	+0.0039	.0.2396	.0.2435	.0000
7	49.64	+0.0002	.0.2433	.0.2435	.0000
8	56.74	-0.0035	.0.2467	.0.2432	-0.0003
9	63.83	-0.0074	.0.2504	.0.2430	-0.0005
10	70.92	-0.0116	.0.2545	.0.2429	-0.0006
11	78.01	-0.0165	.0.2591	.0.2426	-0.0009
12	85.10	-0.0227	.0.2652	.0.2425	-0.0010
13	92.20	-0.0323	.0.2754	.0.2431	-0.0004
14.1	100.00		.0.3339		

Average $E'_o = +0.2435$

TABLE X.—*Electrode potentials of mixtures of indigo trisulphonate (No. 23) and the reduction product, each added in 0.006 M solution to 50 c. c. buffer:*

Buffer No.	pH.	Reduct-ant.	Oxi-dant.	E_h	E'_o	π_h	$E'_o - \pi_h$
2.....	1.419	c. c.	c. c.				
		7	3	0.2351	0.2462		
		5	5	.2464	.2464		
		5	5	.2465	.2465		
		3	7	.2581	.2470		
					0.2465	-0.0853	0.3318
2.....	1.419	7	3	0.2347	0.2458		
		6	4	.2414	.2467		
		5	5	.2464	.2464		
		4	6	.2523	.2470		
		3	7	.2579	.2468		
					0.2465	-0.0853	0.3318
3.....	2.035	7	3	0.1988	0.2009		
		5	5	.2007	.2007		
		4	6	.2152	.2099		
		3	7	.2212	.2101		
					0.2099	-0.1223	0.3322
9.....	5.198	5	5	0.0199	0.0199		
		5	5	.0200	.0200		
					0.0200	-0.3124	0.3324

Average = 0.3321

TABLE XI.—*Potentials of fixed mixture of reduced and oxidized indigo trisulphonate (No. 23) in buffers of different pH.*

FIRST SERIES.

Buffer No.	pH	π_h	E_h	E'_o
1	1.124	-0.0676	+0.2660	+0.2653
3	2.035	-0.1223	+0.2106	+0.2099
7	3.914	-0.2353	+0.0939	+0.0932
13	6.293	-0.3782	-0.0447	-0.0454
14	6.978	-0.4194	-0.0792	-0.0799
15	7.520	-0.4520	-0.1035	-0.1042
19	7.801	-0.4690	-0.1027	-0.1031

SECOND SERIES.

2	1.419	-0.0853	+0.2479	+0.2465
7	3.914	-0.2353	+0.0953	+0.0929
20	8.121	-0.4881	-0.1140	-0.1154
22	9.320	-0.5597	-0.1512	-0.1556
26	10.905	-0.6608	-0.2151	-0.2168
28	12.250	-0.7363	-0.2733	-0.2747

ELECTRODE MEASUREMENTS OF THE DISULPHONATE.

In Clark's (1920) preliminary paper on the reduction potentials of dyes, measurements on a repurified commercial "Indigo sodium sulphonate dye" were given. Clark accepted a reported analysis as that of a monosulphonate when the solubility of the material should have awakened his suspicion. We fortunately have a sample of this same material (A 1919) and find it to be the disulphonate.

In Table XII are the results of titrating this material (after reduction) with ferricyanide and applying the correction for change in acidity. These data are plotted in Figure 2.

In Table XIII are similar data for our new preparation No. 20.

A titration of reduced preparation No. 20 with chromate, not corrected for change of pH, gave deviations less than those found with the tetrasulphonate (Table III).

In Tables XIV and XV are data obtained by the method of mixtures. The pH : E'_o curve is shown in Figure 3, curve 2.

TABLE XII.—Reduced indigo disulphonate (A 1919) titrated with K_3FeCy_6 .

[5 c. c. approx. 0.006 M dye added to 50 c. c. buffer No. 7. pH of 50+5 dilution=3.908.]

K_3FeCy_6	Oxidation.	$\frac{RT}{2F} \ln \frac{[S_r]}{[S_o]}$	E_h	E'_o	Acid correction.	E'_o corrected.	Deviation.
c. c.	Per cent.						
0	0		-0.033				
1	5.92	+0.0361	+0.0196	+0.0557	-0.0003	(+0.0554)	
2	11.83	+0.0263	.0307	.0570	-0.0005	.0565	+0.0001
3	17.75	+0.0200	.0372	.0572	-0.0008	.0564	.0000
4	23.67	+0.0153	.0421	.0574	-0.0010	.0564	.0000
5	29.58	+0.0113	.0465	.0578	-0.0013	.0565	+0.0001
6	35.50	+0.0078	.0503	.0581	-0.0016	.0565	+0.0001
7	41.42	+0.0045	.0539	.0584	-0.0018	.0566	+0.0002
8	47.34	+0.0014	.0572	.0586	-0.0020	.0566	+0.0002
9	53.25	-0.0017	.0605	.0588	-0.0023	.0565	+0.0001
10	59.17	-0.0048	.0639	.0591	-0.0026	.0565	+0.0001
11	65.09	-0.0081	.0673	.0592	-0.0028	.0564	.0000
12	71.01	-0.0117	.0711	.0594	-0.0031	.0563	-0.0001
13	76.93	-0.0157	.0753	.0596	-0.0034	.0562	-0.0002
14	82.84	-0.0205	.0803	.0598	-0.0036	.0562	-0.0002
15	88.76	-0.0270	.0870	.0600	-0.0039	.0561	-0.0003
16	94.68	-0.0376	.0880	.0604	-0.0041	.0563	-0.0001
16.9	100.00		.23				

Average $E'_o = +0.0564$

$\pi_h = -0.2349$

$E_s = 0.2913$

TABLE XIII.—Reduced indigo disulphonate (No. 20) titrated with K_3FeCy_6 .

[5 c. c. approx. 0.006 M dye added to 50 c. c. buffer No. 7. pH of 50+5 dilution=3.911.]

K_3FeCy_6	Oxidation.	$\frac{RT}{2F} \ln \frac{[S_r]}{[S_o]}$	E_h	E'_o	Acid correction.	E'_o corrected.	Deviation.
c. c.	Per cent.						
0	0		-0.03				
1	6.20	+0.0353	+0.0190	+0.0543	-0.0003	(+0.0540)	-0.0022
2	12.58	+0.0253	.0301	.0554	-0.0005	(.0549)	-0.0013
3	18.87	+0.0190	.0372	.0562	-0.0008	(.0554)	-0.0008
4	25.16	+0.0142	.0425	.0567	-0.0010	(.0557)	-0.0005
5	31.44	+0.0102	.0471	.0573	-0.0013	.0560	-0.0002
6	37.74	+0.0065	.0512	.0577	-0.0015	.0562	.0000
7	44.02	+0.0031	.0549	.0580	-0.0018	.0562	.0000
8	50.31	-0.0002	.0585	.0583	-0.0020	.0563	+0.0001
9	56.60	-0.0035	.0621	.0586	-0.0023	.0563	+0.0001
10	62.89	-0.0069	.0657	.0588	-0.0026	.0562	.0000
11	69.18	-0.0106	.0697	.0591	-0.0028	.0563	+0.0001
12	75.47	-0.0147	.0740	.0593	-0.0031	.0562	.0000
13	81.76	-0.0196	.0791	.0595	-0.0034	.0561	-0.0001
14	88.05	-0.0261	.0857	.0596	-0.0036	.0560	-0.0002
15	94.34	-0.0367	.0963	.0596	-0.0039	(.0557)	-0.0005
15.9	100.00						

Average $E'_o = 0.0562$

$\pi_h = -0.2351$

$E_s = 0.2913$

TABLE XIV.—Potentials of mixtures of indigo disulphonate (No. 20) with the reduction product, each added in 0.006 M solution to 50 c. c. buffer.

Buffer No.	pH	Reductant.	Oxidant.	E_h	E'_o	π_h	E_o
2	1.420	c. c.	c. c.	0.1944 .1929 .2033 .2078 .2162 .2163	0.2055 (.2040) .2033 (.2018) .2031 .2052		
		7 7 5 5 3 3	3 3 5 5 7 7		0.2033	-0.0854	0.2907
2	1.420	5 5 4	5 5 6	0.2039 .2035 .2117	0.2050 .2035 (.2014)		
					0.2037	-0.0854	0.2911
3	2.035	7 5 3	3 5 7	0.1575 .1685 .1798	0.1689 .1685 .1687		
					0.1683	-0.1223	0.2909
8	4.558	7 5 3	3 5 7	+0.0053 +0.0154 +0.0277	+0.0164 +0.0164 +0.0166		
					+0.0165	-0.2740	0.2905
10	5.837	7 5 3	3 5 7	-0.0711 -0.0393 -0.0483	-0.0599 -0.0593 -0.0597		
					-0.0596	-0.3508	0.2912

Average $E_o = 0.2909$

TABLE XV.—Potentials of fixed mixture of indigo disulphonate (No. 17) and reduced indigo disulphonate in solutions of different pH.

[10 c. c. 0.005 M dye mixture + 50 c. c. buffer solution.]

Buffer No.	pH	π_h	E_h	E'_o
1	1.138	-0.0684	+0.2257	+0.2228
7	3.928	-0.2361	+0.0559	+0.0530
8	4.556	-0.2738	+0.0198	+0.0169
9	5.183	-0.3115	-0.0189	-0.0218
11	5.978	-0.3593	-0.0647	-0.0576
13	6.268	-0.3767	-0.0837	-0.0866
14	6.975	-0.4192	-0.1205	-0.1234
15	7.519	-0.4519	-0.1458	-0.1487
18	7.566	-0.4547	-0.1370	-0.1399
19	7.804	-0.4690	-0.1466	-0.1495
20	8.126	-0.4884	-0.1571	-0.1600
21	8.702	-0.5230	-0.1790	-0.1819
22	9.309	-0.5595	-0.2015	-0.2044
23	10.200	-0.6134	-0.2325	-0.2354
25	10.075	-0.6055	-0.2229	-0.2258
26	11.018	-0.6622	-0.2546	-0.2575
27	11.699	-0.7031	-0.2762	-0.2791
29	12.280	-0.7380	-0.2993	-0.3022
30	12.564	-0.7551	-0.3116	-0.3145

ELECTRODE MEASUREMENTS OF THE MONOSULPHONATE.

The potassium monosulphonate of indigo is but slightly soluble in water. A solution saturated at room temperature would be sufficiently concentrated for our purposes, but when this is even highly diluted with salt solutions a slow precipitation occurs. Conse-

quently the potential of an adequately buffered mixture of the oxidant and reductant drifts while the oxidant is leaving the solution.⁵ Initial potentials of mixtures and rapid measurements in titration must therefore be the rule. Nevertheless, the approximate position of the system may be estimated, as will be shown.

A saturated solution of potassium indigo monosulphonate was reduced, filtered, and stored by means of the apparatus shown in Figure 3 of the previous paper of this series, and modified as previously described. Ten c. c. of this solution were added to 50 c. c. O_2 -free buffer and then titrated with a mixture of 10 c. c. water + 50 c. c.

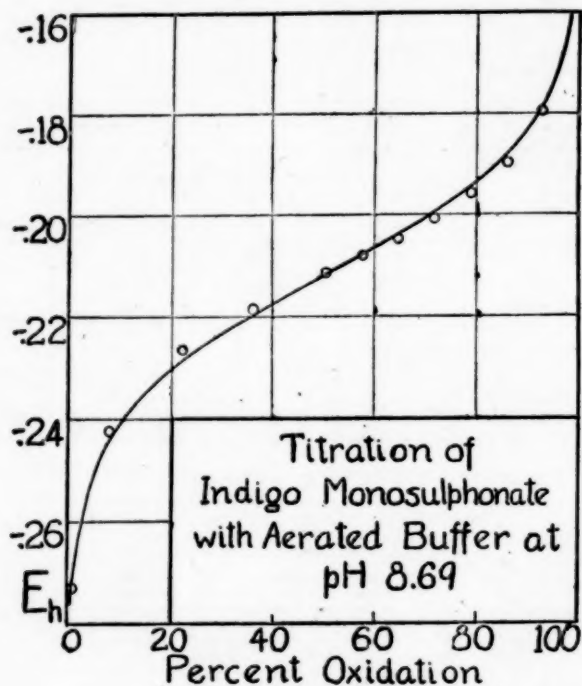


FIG. 1.

of the same buffer containing the oxygen it had taken up on standing in the air. In the titration with buffer No. 21, 14 c. c. were required. In Figure 1 the data are plotted with percentage oxidation against observed E_h values. It is seen at once that although the deviations from the ideal curve (shown as unbroken line) are considerable they are not serious.

The average E'_o value calculated from the data of this titration was -0.2112 , and the pH value of the buffer solution was 8.69. A similar titration was made with aerated buffer No. 26, pH=11.11, and there was found an average E'_o value of -0.2921 .

⁵The same difficulty was encountered by Holmes (1923) in spectroscopic studies.

Using initial potentials as the safest, there were found by the method of mixtures the data in Tables XVI and XVII. In Figure 3 is plotted the $\text{pH} : E'_o$ curve.

TABLE XVI.—Potentials of mixtures of indigo monosulphonate (No. 5A) and the leuco-compound, each of same concentration and added to 50 c. c. buffer.

Buffer No.	pH	Reductant	Oxidant.	π_h	E_h	E'_o	$E'_o - \pi_h$
3	2.034	c. c. 5	c. c. 5	-0.1222	+0.1390	+0.1390	0.2612
9	5.150	6	4	-0.3095	-0.0515	-0.0494	0.2619
		6	4		-0.0537	-0.0486	
		5	5		-0.0476	-0.0476	
		4	6		-0.0425	-0.0476	
21	8.604	5	5	-0.5225	-0.2083	-0.2083	
26	11.111	5	5	-0.6678	-0.2911	-0.2911	
		5	5		-0.2903	-0.2903	
						-0.2907	

Average $E_o = 0.2618$

TABLE XVII.—Potentials of a fixed mixture of indigo monosulphonate (No. 5A) and its leuco-compound at different pH values.

FIRST SERIES.

Buffer No.	pH	π_h	E_h	E'_o
1	1.138	-0.0684	+0.1856	+0.1932
7	3.928	-0.2361	+0.0182	+0.0258
15	7.519	-0.4519	-0.1912	-0.1836
19	7.791	-0.4683	-0.1829	-0.1753
23	10.107	-0.6074	-0.2672	-0.2596
28	12.264	-0.7370	-0.3328	-0.3252

SECOND SERIES.

1	1.138	-0.0684	+0.1797	+0.1925
3	2.045	-0.1229	+0.1249	+0.1377
5	2.817	-0.1693	+0.0767	+0.0895
9	5.197	-0.3124	-0.0633	-0.0505
14	6.975	-0.4192	-0.1682	-0.1564
21	8.699	-0.5228	-0.2198	-0.2070
25	9.936	-0.5972	-0.2691	-0.2563

General Discussion.

The results of the preceding measurements may be intercompared with the aid of graphic representations.

In Figure 2 are shown comparable titrations with ferricyanide. Since the pH values of the solutions were essentially the same, Figure 2 reveals the relative spacing of the systems for an acid medium. For comparative purposes there is introduced the percentage oxidation: E_h curve of the monosulphonate calculated for the same pH from the characteristics of this system as determined

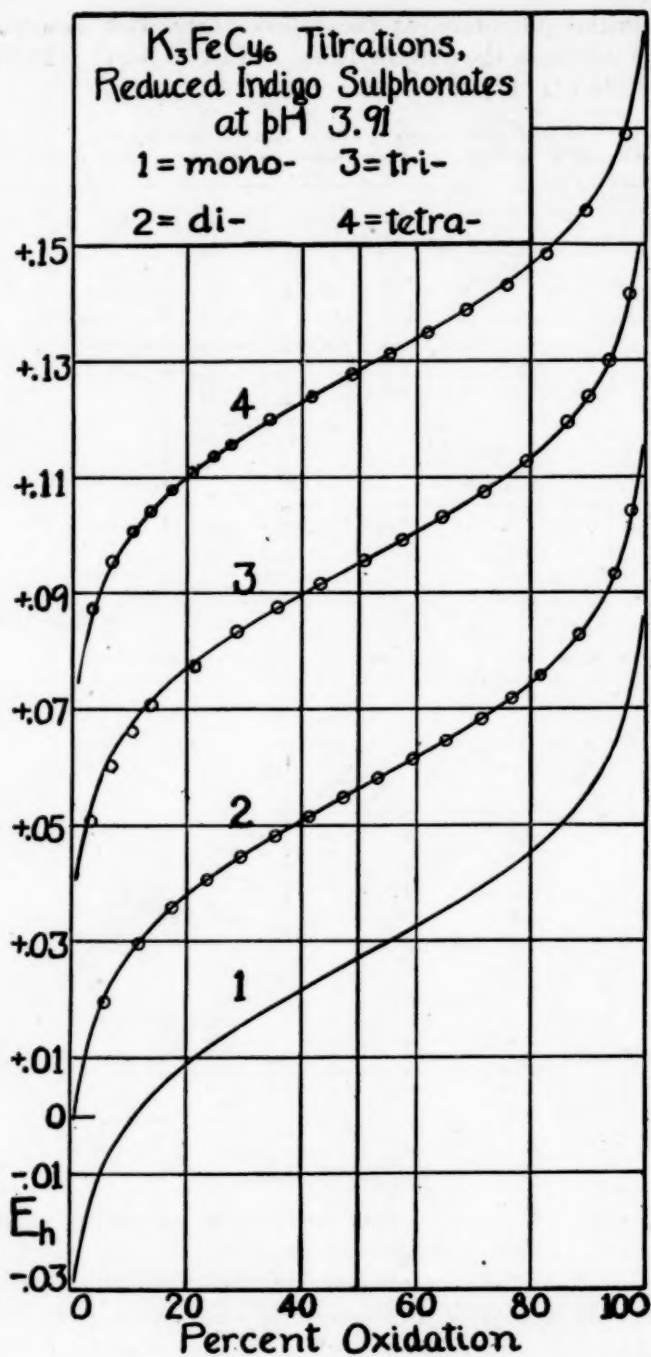


FIG. 2.

by other means. In the other curves experimental data are indicated by circles. The conformity to the type curve shows clearly that the number of electrons concerned is 2 and that the experimental data are reasonably precise.

In Figure 3 are shown the E'_o :pH curves. The experimental data obtained by the method of mixtures are shown by dots and

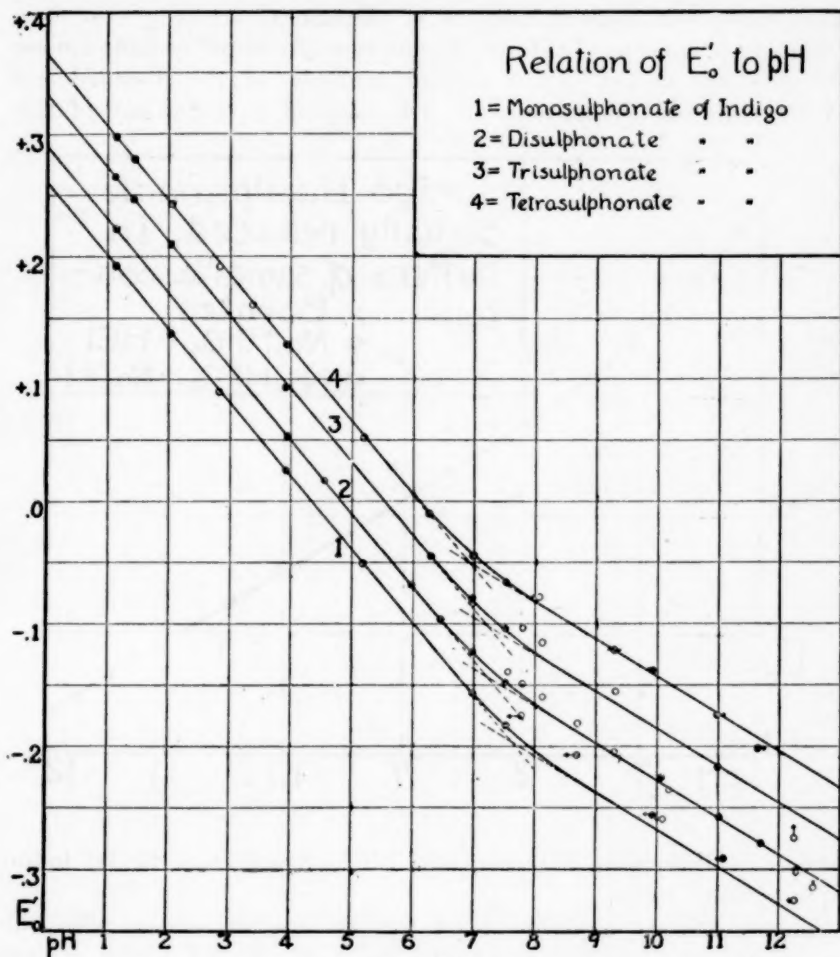


FIG. 3.

circles, the alternation of these indicating successive changes in buffer system as shown by the grouping in Table II. So far as can be revealed on a small chart the alignment is fairly good in the acid region and conforms to the line for which $\frac{dE}{dpH} = -0.0601$. In the alkaline region the discrepancies are large but leave evidence that the theoretical curve is a line for which $\frac{dE}{dpH} = -0.03006$. On this

assumption we have constructed a stencil of the type curve derived from the equation to be given presently, and with this we have drawn the curves shown. These curves are drawn close to the points determined with phosphate mixtures near pH7. The discrepancies with the borate buffers (circles) next in series then appear large, but if the type curve be moved to include the borate data more reliable data are thrown out of alignment.

Sooner or later in the study of oxidation-reduction systems among the dyes we should expect to find examples of the so-called salt effect, and perhaps material as well adapted to the study of this

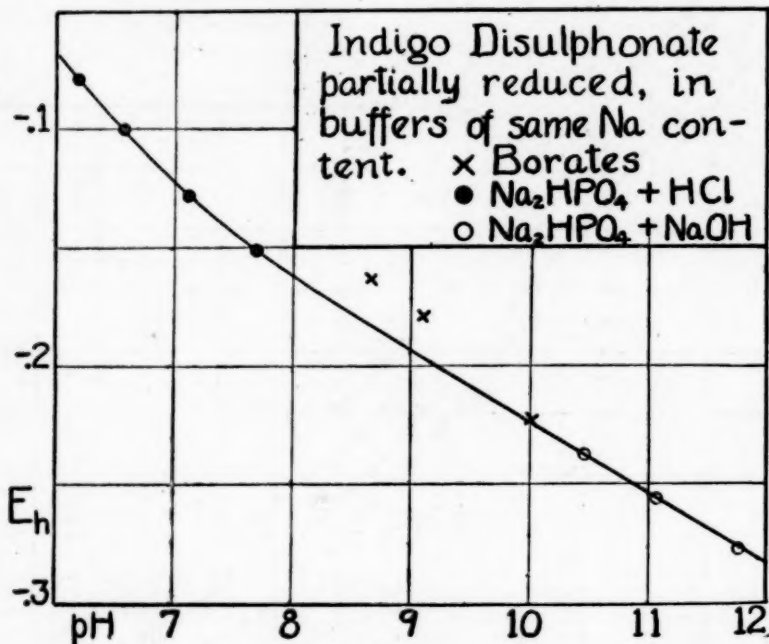


FIG. 4.

subject as Sørensen, Sørensen and Linderstrøm-Lang (1921) found quinhydrone to be.

A preliminary experiment on this subject was made with the solutions listed in Table XVIII. In Table XVIII under π_h are given the hydrogen electrode potentials of the solutions. Under E_h are the electrode potentials obtained when to 50 c. c. of buffer were added 5 c. c. of an approximately half-reduced solution of indigo disulphonate. Were there no salt effect, $E_h - \pi_h$ should be the same in each case. The variations are not large enough to speculate upon, but suggest a salt effect which should be investigated more carefully, especially with solutions of high pH. Such an investigation would involve several series of control measurements,

for it will be understood that hydrogen electrode measurements of dye-free buffers are made the basis of pH calculations, and there is no direct way of estimating the small effect of the dyes themselves on the pH of the solution.

TABLE XVIII.—*Partially reduced indigo disulphonate in buffer solutions of different total salt content.*

Solution.	π_h	E_h	$E_h - \pi_h$
250 c. c. M/5 KH phthalate+750 c. c. H ₂ O+0 c. c. M/5 KCl	-0.2393	+0.0543	+0.2933
250 c. c. M/5 KH phthalate+725 c. c. H ₂ O+25 c. c. M/5 KCl	-0.2384	+0.0551	+0.2935
250 c. c. M/5 KH phthalate+650 c. c. H ₂ O+100 c. c. M/5 KCl	-0.2369	+0.0558	+0.2927
250 c. c. M/5 KH phthalate+500 c. c. H ₂ O+250 c. c. M/5 KCl	-0.2351	+0.0574	+0.2925

It has not been our intention to examine the possible salt effect except in cases where it becomes large enough to obscure those main features of a system formulated by the elementary treatment given in our second paper. We are now confronted with the problem of dealing with the peculiar data found with borate solutions. The effect is far beyond the range of experimental error and is evident in Figure 3, where the borate data are shown by circles situated to the right of the bend in each curve. It is even more striking in Figure 4, which represents a series of E_h measurements made with a partially reduced disulphonate solution introduced into buffers of uniform sodium content. The alignment with the type E_h :pH curve is excellent with the phosphate mixtures, but two of the borates give large displacements.

The first thought that occurs is that indigo and boric acid form a complex comparable with the well-known boric acid-mannitol complex, or with one of those numerous complexes used by Böeseken (1921) in the study of isomerism. Were such an effect demonstrated it would suggest a very interesting structure for indigo. A comparatively crude experiment, however, shows that our apparent displacement of electrode potentials can not be entirely due to a decrease in pH resulting from a boro-indigo-white complex which is comparable to the boro-mannitol complex. To 5 c. c. de-aerated water containing 10 drops phenol red were added 5 c. c. reduced, 0.006 M indigo disulphonate. Under nitrogen protection this mixture was titrated with dilute alkali and the pH at each stage of alkalization was measured colorimetrically with the aid of a comparator. A similar experiment was made with a mixture of reduced indigo disulphonate and boric acid. Within the limits of the method (0.05 pH unit) no difference in the two titration curves was detected. With comparable conditions a boric acid-mannitol combination gave the well-known displacement.

This is a crude experiment and should be repeated with refinements and with the unreduced compounds; but it is sufficient to show that the effect of a boro-indigo-white complex, if it exists, is not sufficient to account for the whole of the displacement in the alignment of our data.

In another experiment the addition of boric acid to a partially reduced tetrasulphonate solution in a region of pH in which boric acid as an acid is inert produced no significant change in potential.

Another experiment, not very well controlled with respect to the effect of the acid indigo-white, indicated that an alteration of the ratio of borate to NaCl should have a large effect.

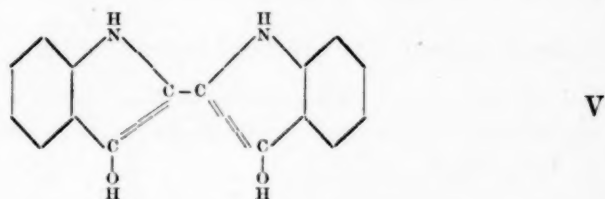
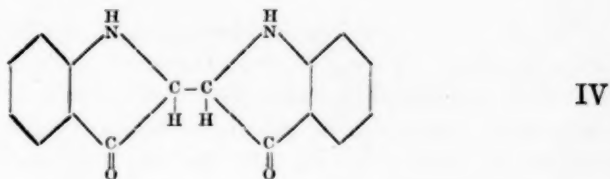
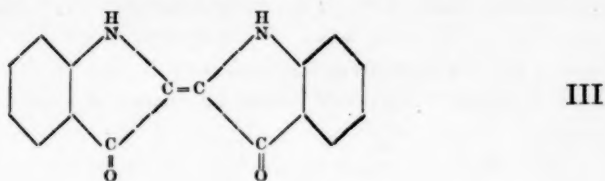
With the data before us at the moment we can not give a rational explanation of the conduct of the indigo sulphonates in borate solutions, but we believe that the problem is a special one outside the present general survey.

If this be granted, it will be admitted that in general the type curves of Figure 3 have been reasonably placed, except for the 0.03 branch of the monosulphonate curve, which falls as it does by reason of the inclusion of phosphate points near pH 7.

Incomplete knowledge of the effects of borate leaves us in considerable uncertainty regarding important portions of the curves shown in Figure 3. We have already stated our reasons for drawing these curves as shown, we have stated our reasons for temporarily neglecting the borate data, and we believe that each curve in Figure 3 represents a first approximation of the relation of E'_0 to pH.

As repeatedly noted in previous papers, there are a number of possible cases to which such a curve will apply, and we must draw upon the chemistry of indigo to define the case.

According to the formula of Baeyer (1883), indigo has structure III and indigo-white structure IV or V.



These represent fairly well certain fundamental facts of indigo synthesis and disruption, but they are not now accepted as representing several physical properties and certain reactions of indigo. Many modifications of the picture have been suggested, but we shall not discuss them, because we are concerned with but one point—the acidic nature of indigo white, to be discussed in more detail presently.

It is generally agreed that indigo-white in the isolated condition has two more hydrogens than indigo. We have shown clearly that two electrons are concerned in the reduction, and it is reasonable to assume that these two electrons create two points potentially anionic, which become seats of hydrogenation in the isolated compound. If so, the case is clearly an example of group A, class 2, outlined in the second paper of this series.

The equation for this case at a temperature of 30° is

$$E_h = E_o - 0.03006 \log \frac{[S_r]}{[S_o]} + 0.03006 \log [K_1 K_2 + K_1 [H^+] + [H^+]^2] \quad (2)$$

Here K_1 and K_2 are the dissociation constants of those points in indigo-white which are created in the act of reduction. We are neglecting the dissociation constants of the sulphonic acid groups in the sulphonated indigos, because, within the range of pH covered by our investigation, there is no evidence of their effect.

Now, while our experiments have not been extended in the alkaline region to the available limit and are somewhat uncertain at the extremes used, there is no indication that the E'_0 :pH curve bends parallel to the pH axis. This means that if equation (2) is applicable the K_1K_2 term is negligible or K_2 is less than 10^{-12} .

For present purposes, then, equation (2) simplifies to (3),

$$E_h = E_0 - 0.03006 \log \frac{[S_r]}{[S_o]} + 0.03006 \log [K_1[H^+] + [H^+]^2] \quad (3)$$

When K_1 is negligible in comparison with $[H^+]$, E_0 can be found directly from $E'_0 - \pi_h$. Values taken from Tables VI, X, XIV, and XVI are assembled in Table XIX. As shown in the second paper of this series, there can be calculated from any E'_0 value and the corresponding pH (e. g., E_0 , pH=0), the hypothetical hydrogen pressure in equilibrium with the system. It was suggested that such hydrogen pressures be expressed in terms of $\log \frac{1}{H_2}$ for which the symbol rH was given. Characteristic of a system is the rH value at 50 per cent reduction and negligible ionization. Such values are given in Table XIX.

TABLE XIX.—"Normal potentials" and characteristic rH values.

System.	E_0	rH
Indigo monosulphonate \rightleftharpoons leuco compound.....	+0.262	8.7
Indigo disulphonate \rightleftharpoons leuco compound.....	+0.291	9.7
Indigo trisulphonate \rightleftharpoons leuco compound.....	+0.332	11.1
Indigo tetrasulphonate \rightleftharpoons leuco compound.....	+0.365	12.1

When E_0 is known, K_1 in each case can be determined graphically as indicated in Figure 3 or by the use of equation (3). If (3) is used for this purpose there should be employed data taken from a region of pH in which there is partial dissociation of the acid. Buffers No. 14 and No. 15 furnish favorable conditions; and with the data of the systems in these solutions were calculated the K_1 values listed in Table XX. These are slightly different from the K_1 values obtained by inspection of the curves in Figure 3. It is unfortunate that measurements in the critical zone of pH are not certain. It is highly desirable that some one refine the measurements till accurate values of K_1 are found, for it will be noted that in the values given there is a very suggestive order* inviting speculation in which we now dare not indulge.

* Among other relations note that Figure 3 suggests that the substitution of each sulphonic acid group causes an equal shift in the potential of the ionized system (alkaline region).

TABLE XX.—*Dissociation constants of leuco-indigo sulphonates.*

Compound.	$\log \frac{1}{K_1}$	K_1	K_2
Leuco-indigo monosulphonate	7.8	1.6×10^{-8}	Less than 10^{-12} .
Leuco-indigo disulphonate	7.3	4.9×10^{-8}	Do.
Leuco-indigo trisulphonate	7.1	7.7×10^{-8}	Do.
Leuco-indigo tetrasulphonate	6.96	11.2×10^{-8}	Do.

With equation (3) and the values for E_0 and K_1 we may calculate the E'_0 values corresponding to the pH values measured, and thus gain a numerical estimate of discrepancies not clearly shown by Figure 4. Illustrating this with the data for the tetrasulphonate we find the E'_0 values shown in the next to the last column of Table VII. The preponderance of the positive sign in the deviations given in the last column of Table VII could be eliminated by slightly shifting the values of E_0 and K_1 , but the deviations given show clearly amid the fair agreement of acid values the large displacement in solution No. 5 and the peculiar deviations in the alkaline solutions.

Similar deviations are found with the other sulphonates and often recur with a regularity, suggesting that they are by no means attributable in their entirety to experimental errors.

We have not dwelt in detail upon all the discrepancies to be found, because, in the first place, they are of an order of magnitude which does not seriously affect the conclusions we draw, and, in the second place, it is difficult to separate experimental error from significant displacement. We may, however, note that there is some suggestion of an effect of total concentration of the dye and its leuco-compound not covered by the demands of the fundamental equations. This, together with the effect of borate, the salt-effects at all ranges of pH, studies at pH ranges higher and lower than those covered by our work, and temperature effects, remains to be investigated in detail and with high precision.

It is evident from Figure 3 that sulphonation progressively shifts the position of the system toward the oxidation side of the scale. Thus the study of oxidation-reduction equilibria furnishes new evaluations of the effect of substitution, as we pointed out in 1921 (*cf.* Cohen and Clark 1921, Sullivan and Clark 1921, LaMer and Baker 1922, and Conant, Kahn, Fieser and Kurtz 1922).

Furthermore, the dissociation constant of the first hydrogen of the leuco compound can be calculated, as pointed out in our second paper and touched upon earlier by Clark and Cohen (1921) and Clark (1922). Here again, as shown in Table XX, the influence of substitution is made evident.

While the subject has not been studied in detail, it is found that colorimetric measurements with indigo sulphonates of the reduction

potentials of bacterial cultures agree substantially with electro-metric measurements.

SOME CONSIDERATIONS OF THE SYSTEM INDIGO \rightleftharpoons INDIGO-WHITE.

The extremely low solubility of indigo itself makes it impracticable to study the system indigo \rightleftharpoons indigo-white by the methods followed with the soluble sulphonates. However, there are a few theoretical aspects which seem worthy of comment.

There is no reason to doubt that the equation which is applicable is identical in structure with that applying to the sulphonates, but with new constants. At 30° the equation is

$$E_h = E_o - 0.03 \log \frac{[S_r]}{[S_o]} + 0.03 \log [K_1[H^+] + [H^+]^2] \quad (4)$$

The solubility of indigo limits the value of $[S_o]$. If there be present the solid phase so that $[S_o]$ may be considered a constant, C , then

$$E_h = E_o + 0.03 \log C - 0.03 \log [S_r] + 0.03 \log [K_1[H^+] + [H^+]^2] \quad (5)$$

It is a somewhat dangerous assumption to consider K_1 to be of the same order of magnitude for indigo-white as for its sulphonates,

but we shall place it at 10^{-8} $\left(\log \frac{1}{K_1} = 8\right)$. Then at two pH units higher

than 8, or at pH 10, 99 per cent of the indigo-white should be ionized and the total solubility should be near the maximum. $[H^+]$ has then become so low in relation to K_1 that equation (5) is reduced to (6), an equation in which all constants have been combined, and which is applicable at alkalinities higher than pH 10.

$$E_h = C' - 0.03 \log [S_r] - 0.03 \text{ pH} \quad (6)$$

It follows at once that the reduction potential of the system will build up to higher and higher negative values as the total indigo-white increases and as pH increases. Conversely, the pH of the solution and the reduction intensity of the system used as reducing agent determine the amount of indigo-white which may be formed.

While this conclusion may be modified by factors which control the solubility of indigo blue, it may be of some significance where it is found necessary to modify the alkalinity and the reducing reagent used in vat dyeing.

It also follows that when the system under consideration is used to determine oxidation-reduction intensities it is necessary not only to know pH as in other cases but also to know $[S_r]$. It is unfortunate that the old conception of a specific "affinity" independent of the

concentration of the reactant was carried by Ehrlich (1885) into the subject now under consideration. For purely histological reasons he chose dyes of low solubility with which to examine the reducing power of tissues and he neglected consequences which we shall comment upon in a later paper. It may here be noted that Oelze (1914) employed colloidal indigo after the manner of Ehrlich and that his results have little quantitative significance for lack of the information which equation (5) shows to be essential.

These theoretical considerations would not be complete without a note to the effect that the potential according to equation (5) varies as a small fraction of the logarithm of the concentration of indigo-white. Consequently, whatever the solubility of indigo may be, the system will probably lie within a fairly well defined, although possibly broad, zone of potential under ordinary conditions.

Our very rough measurement of this was made as follows: Twenty milligrams of Kahlbaum's indigo were suspended in 50 c. c. water containing 0.7 c. c. 0.2 N NaOH and some platinized asbestos. Hydrogen was bubbled through this mixture over night. It was then evident that reduction was not complete. The solution was filtered into a protected pipette.

It may be assumed that after 16 hours' stirring with the hydrogen stream and incomplete reduction of the indigo the filtrate was saturated with indigo. There was a slight green cast to the yellow color of the filtrate. It was expected that a dilution of 1 part of this solution to 100 parts of buffer would be sufficient to make the solution unsaturated with respect to indigo. By sufficiently careful titration it would then have been possible to determine from the flattening of the titration curve the approximate saturation point for the indigo (*cf.* Clark, 1920). But on attempting to titrate this very dilute solution, the potentials were found to be very uncertain. The system acted as if saturated with indigo from the very first and as if this indigo were being steadily precipitated by the buffer salts with a consequent slow drift toward a more negative electrode potential. On the addition of oxidizing agents there was no evidence of any marked change of potential, but only of the small shift expected in a system already saturated with oxidant. Had the system not been saturated with oxidant at the start of the titration, the 0.1 per cent of the total calculated oxidizing agent required to oxidize the reductant, which was the amount first added, should have given a decided change in potential. Since no such change was observed, we can assume that the oxidant present was less than 0.1 per cent of the reductant.

The reductant was determined to be about 0.0008 molar, and if the oxidant already saturated the buffer solution at the suggested

small percentage of this concentration, the solubility of indigo itself must be so low that it is determined by grain size.

When 5 c. c. of the solution were added to 100 c. c. buffer No. 26 (pH 11), E_h was about -0.40 . When 5 c. c. were added to 100 c. c. buffer No. 14 (pH=7.0), E_h was about -0.25 .

If we take the liberty of using these two very rough measurements to place the type curve as found in Figure 3, they would give $K_1 = 10^{-8}$.

What E_o is can only be guessed. If we assume the oxidant to have been as high as 1 per cent of the reductant, $E_o = +0.23$ volt, a value 0.03 volt more negative than that found for the mono sulphonate. If the percentage oxidant were lower than the 0.1 per cent suggested above, the system would fall amid the sulphonates.

Titration yielded no steady potentials, probably because of the salting out of the oxidant. An experiment in which the buffer salt was lowered to 0.01 molar gave no improvement.

It is probable that the system is situated near the zone of the indigo sulphonates, as our rough measurements suggest.

ON THE ACIDIC NATURE OF THE LEUCO-COMPOUNDS.

Whatever the difficulties may be in accounting for the effect of borate solutions as revealed in Figures 3 and 4, it is very evident that the curve relating E'_o to pH has two distinct branches. On one, E'_o varies 0.06 volt for each unit change in pH; and on the other, E'_o varies about 0.03 volt for each unit change in pH. This was accounted for in the previous section on the assumption that when the hydron concentration is lowered to a region below 10^{-7} , there is ionization of one and only one of the two potentially acidic groups created in the reduction. The question now arises whether there is at hand a method for confirming this conclusion.

The most direct method would be to titrate a reduced indigo sulphonate solution with alkali and determine the acid-base equilibrium curve by the usual method. For this purpose the hydrogen electrode is precluded on theoretical grounds, although it might be operated with certain precautions. At first thought it might seem to be begging the question to employ the electrode potentials of a mixture of reduced and oxidized indigo sulphonate. However, it is reasonable to assume that the only large change in this potential which could be caused by addition of alkali, must be due to a change in acid-base equilibrium. If then it can be shown that there is a buffering effect before one equivalent of alkali is added to a solution of reduced indigo sulphonate, and a jump in potential at one equivalent, the presumption is that the presence of one acidic or basic group has been demonstrated. Of the alternative acid or basic

group, we shall consider the group in question to be acidic for reasons which are not conclusive but which are generally accepted.⁷

In the following experiment a definite mixture of reduced and oxidized indigo tetrasulphonate was added to an unbuffered salt solution. Oxygen-free acid or alkali was then added in steps and the potentials were measured. The original data are given in Tables XXI and XXII, so that the reader may plot these and determine for himself the essential point, namely, that there is evidence of the neutralization of one and only one equivalent of alkali. To make this clearer we shall use our previous data without involving the assumptions intended to be proved. The observed values of E_h are first transformed to E'_o values by using the known ratio of reductant to oxidant. Then, without reference to the equation involving the acid dissociation constant, by use of the graph relating the experimental values of E'_o to pH, there is estimated the pH value corresponding to each of the values of E_h observed in the acid-base titration.

TABLE XXI.—Titration of 25 c. c. 0.00285 *M* reduced indigo tetrasulphonate + 4 c. c. 0.00285 *M* indigo tetrasulphonate + 25 c. c. 0.2 *M* KCl with 0.01 *N* NaOH. (7.12 c. c. NaOH=1 equivalent.)

NaOH	Neutralization.	E_h	E'_o	pH	pH calculated $K_a=10^{-7}$
c. c.	Per cent				
0	0	+0.0332	+0.0572	5.13	-----
0.5	7.02	-0.0101	+0.0139	5.88	5.88
1.0	14.04	-0.0283	-0.0043	6.20	6.22
1.5	21.07	-0.0396	-0.0156	6.40	6.42
2.0	28.09	-0.0483	-0.0243	6.58	6.59
2.5	35.11	-0.0554	-0.0314	6.72	6.74
3.0	42.14	-0.0617	-0.0377	6.85	6.86
4.0	56.18	-0.0731	-0.0491	7.12	7.10
5.0	70.22	-0.0842	-0.0602	7.41	7.37
6.0	84.27	-0.0975	-0.0735	7.78	7.72
6.5	91.30	-0.1067	-0.0827	8.05	8.00
6.8	95.51	-0.1138	-0.0898	8.27	8.27
7.0	98.31	-0.1196	-0.0956	8.44	8.80
7.2	101.1	-0.1271	-0.1031	8.70	-----
7.6	105.7	-0.1429	-0.1189	9.20	-----
8.0	112.4	-0.1545	-0.1305	9.60	-----
8.5	119.4	-0.1657	-0.1417	9.96	-----
9.0	126.4	-0.1743	-0.1503	10.24	-----
10.0	140.4	-0.1861	-0.1621	10.64	-----
11.0	154.5	-0.1943	-0.1703	10.90	-----
13.0	182.6	-0.2054	-0.1814	11.16	-----
15.0	210.7	-0.2127	-0.1887	11.35	-----
20.0	280.9	-0.2237	-0.1997	11.60	-----

⁷ In the voluminous literature on indigo are many conceptions of the acid-base character of indigo which we shall not pause to compare.

TABLE XXII.—*Titration of 25 c. c. 0.00285 M reduced indigo tetrasulphonate + 4 c. c. 0.00285 M indigo tetrasulphonate + 25 c. c. 0.2 M KCl with 0.01 N HCl. (7.12 c. c. HCl would equal 1 equivalent of base if present.)*

HCl	E _h .	E'.	pH
c. c.			
0	+0.0315	+0.0554	5.17
0.5	.0882	.1121	4.22
1.0	.1091	.1330	3.87
1.5	.1209	.1448	3.68
2.0	.1290	.1529	3.55
3.0	.1394	.1633	3.35
4.0	.1469	.1708	3.25
6.0	.1569	.1808	3.08
8.0	.1637	.1876	2.97
10.0	.1688	.1927	2.88
14.0	.1761	.2000	2.76
20.0	.1833	.2072	2.64

Knowing the amount of reduced indigo sulphonate used, we can calculate the percentage of one equivalent of alkali or acid added at each stage of the titration. With these data the familiar acid-base titration curve can be plotted.

In Figure 5 there is shown such a curve for reduced indigo tetrasulphonate. Twenty-five c. c. of a 0.002 molar solution of reduced indigo tetrasulphonate were employed, and the electrode potential was stabilized by the definite ratio of oxidant to reductant obtained by addition of 4 c. c. of the oxidant. These quantities were added to 25 c. c. M/5 KCl and then titrated with oxygen-free 0.01 N NaOH in one case and oxygen-free 0.01 N HCl in the other. The calculated percentages neutralization are plotted as abscissas. The pH values, plotted as ordinates, were estimated graphically as described above. The experimental data are plotted as circles. To aid in the interpretation of this chart there is drawn a type titration curve of an acid having a dissociation constant of 10^{-7} . This is spread between zero percentage neutralization and the 100 per cent neutralization of one equivalent. The second curve to the left is that of a series of hydrogen electrode measurements on the titration of a solution similar to the KCl-dye solution, except that the relatively small concentration of dye was replaced by K_2SO_4 , the K of which was equivalent to the K of the organic compound. This curve is placed to represent approximately the course to be followed after the alkali had neutralized the one available hydrogen of the reduced indigo tetrasulphonate. To the right of zero per cent neutralization is the curve of hydrogen electrode measurements on the KCl- K_2SO_4 mixture titrated with acid. The dots represent the course followed on titrating reduced indigo tetrasulphonate.

At the higher pH values there is nonconformity between expected and found courses of the titration, due, probably, to uncertainty in pH:E' curve at high alkalinities. The discrepancy is against the assumption of any second acidic group. A conclusion on this point

is unwarranted because of the uncertainties of measurement, but it is safe to say that if there is a second acidic hydrogen, its dissociation constant is less than 10^{-12} . Except for the discrepancy in the more alkaline region, the observed and estimated courses of the titration agree.

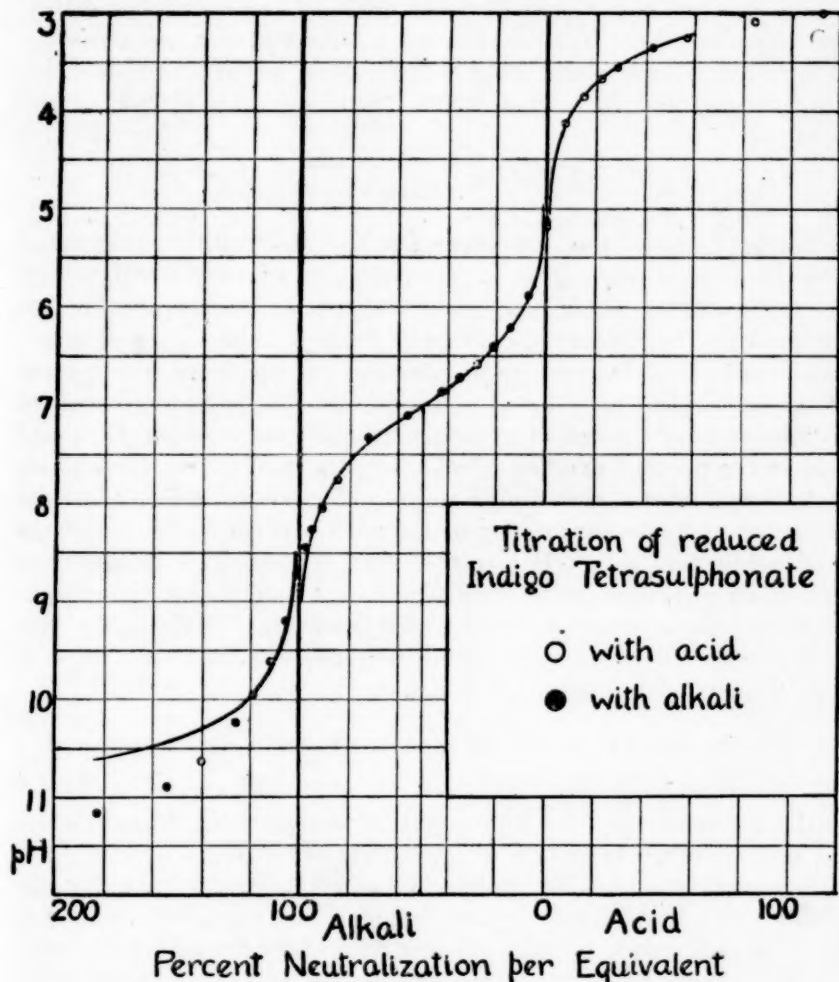


FIG. 5.

Experiments similar to the acid and base titrations of the tetrasulphonate were made with the "di-" and "tri-" sulphonates and with like results. In another experiment with the disulphonate the proportions of disulphonate and reduced disulphonate were reversed to reveal any buffer effect due to the acid or base groups in the oxidant. None within the limits which can be plainly revealed by the method was found. Experiments without KCl and at greater extremes of

acidity and alkalinity would probably reveal acid or basic properties not included in our discussion.

Assigning to the group created by the reduction of indigo sulphonates a dissociation constant of the order of magnitude of 10^{-7} , we may conclude that the group is practically completely ionized at alkalinities higher than pH 10. For those who care to insist that in the reduction of indigo an actual and complete hydrogenation occurs as an intermediate step, there is still ample latitude; but it is interesting to note that in a 0.0001 molar solution at pH 12 the equation

$$\text{pH} = \log \frac{1}{K_a} + \log \frac{\text{anion}}{\text{undissociated residue}}$$

indicates that on the statistical average the fully hydrogenated product can be present in a concentration of only 0.000,000,001 molar. In other words, while two electrons or their equivalent are required for the reduction, only one hydrogen is incorporated in the molecule at moderately high alkalinities. While there is no reason to doubt that indigo-white as isolated from solution is hydrogenated to the extent of 2 atoms of hydrogen, it would be erroneous to regard this as the product existing in alkaline solutions.

As is well known, the sulphonates of indigo are reversible acid-base indicators. As determined by us the pH range for the disulphonate is, roughly, blue at pH 11.6 to yellow at pH 14. The instability of potentials in this range (accounted for by a progressive, irreversible change in the system) has prevented a thorough investigation of this region. We therefore have insufficient experimental data to contribute to this phase of the problem.

ON THE POSSIBILITY OF ANALYZING A MIXTURE OF THE SULPHONATES OF INDIGO.

Having placed with a fair degree of accuracy the curve relating E_h to percentage reduction at any given pH in the case of each of the four sulphonates of indigo, we can compute graphically the resultant titration curve for any mixture. It remains to be determined whether such a resultant curve differs from the type sufficiently to characterize the mixture, and whether the experimental measurements can be made accurate enough to conform to the requirements of analysis.

Two-component mixtures resulting from undersulphonation are probably most frequently encountered. We shall consider the case of a trisulphonate contaminated with disulphonate and shall illustrate a graphic method of treatment.

In the titration of an unknown mixture, E_h would be plotted against percentage oxidation or reduction of the whole. In Figure 6

the abscissa is this percentage. If now the molecular ratio of disulphonate to trisulphonate is 15/85, and the reduced disulphonate could be titrated separately, it would give curve A; while the trisulphonate, if it could be titrated separately and after the disulphonate, would give curve B. The centers of curves A and B are 0.041 volt apart (see Table XX), if the titration be performed in an

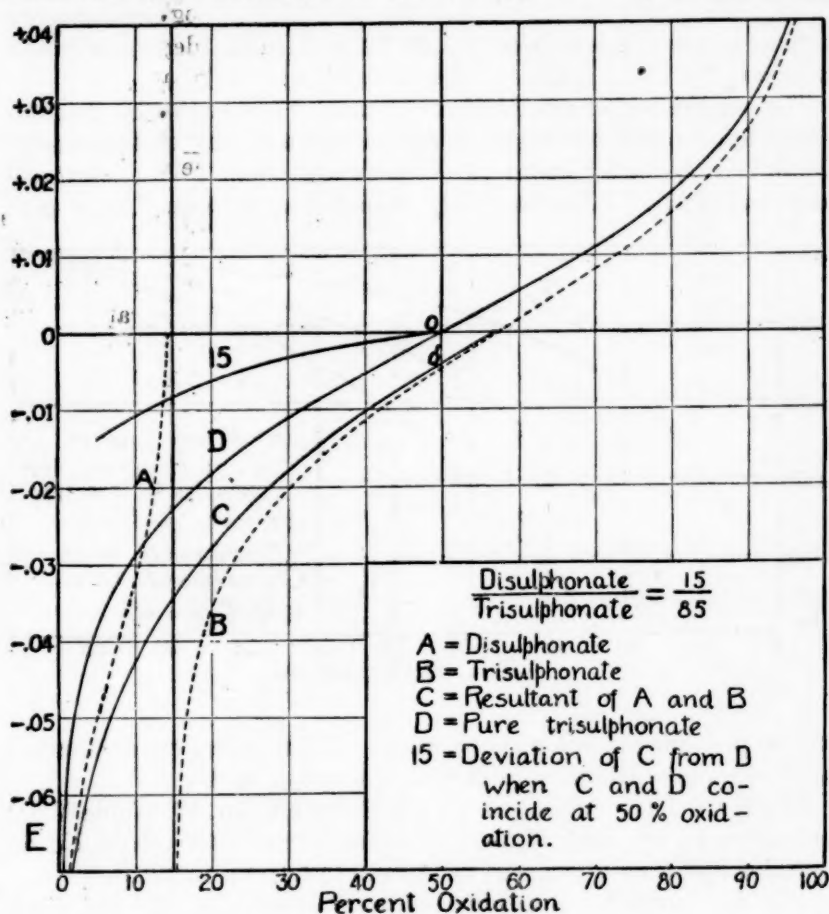


FIG. 6.

acid medium. For convenience we have centered B at $E_h = 0$, since our object is to obtain a deviation curve.

The actual titration curve would be a resultant of A and B, namely, C. In dealing with an experimental C curve, let its center, O' , be determined graphically. The displacement ($O - O'$) of this center from that of a pure trisulphonate curve (D), would be valuable were it not that the significance of this displacement would be found only by extremely accurate control of pH. We shall therefore neglect this

and shall consider the divergence of the type curve, D, from C when both are given a coincident point at 50 per cent oxidation of the whole. The deviation curve so determined is shown by the curve marked 15.

By a similar procedure, but on an enlarged scale, there were determined the deviation curves for the molecular ratio $\frac{\text{disulphonate}}{\text{trisulphonate}}$ in cases in which this ratio is 5/95, 10/90, and 15/85. These are shown in Figure 7.

The summation of graphical errors and of the large experimental errors for small percentages oxidation make it unwise to consider the deviations below about 15 per cent oxidation. We have therefore transferred to Figure 7 only data falling between 15 per cent

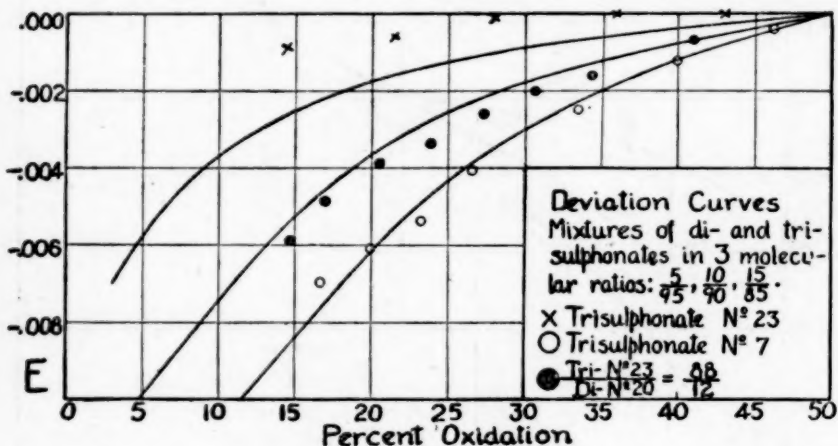


FIG. 7.

and 50 per cent oxidation of the whole. These data were determined by ferricyanide oxidation as described on page 1681.

In Figure 7 the deviations for trisulphonate No. 23 (Table VIII) are shown by crosses. If the method be correct, preparation No. 23 contains less than 2 per cent disulphonate or its equivalent.

The deviations for a mixture of trisulphonate No. 23 and disulphonate No. 20 (Table XXIII) are shown by dots. The mixture was prepared on a weight-percentage basis. When corrected for different moisture contents of the two substances, the molecular ratio was calculated to be $\frac{\text{disulphonate}}{\text{trisulphonate}} = \frac{12}{88}$. The deviation data of Figure 7 are in substantial agreement with this ratio.

TABLE XXIII.—Titration of mixture of reduced di- and tri-sulphonates of indigo with ferricyanide in buffer No. 7. Molecular ratio $\frac{di}{tri} = \frac{12}{88}$.

K ₂ FeCy ₆	Oxidation.	RT 2F ln $\frac{[S_2]}{[S_0]}$	E _h .	E'.	Acid correction.	E' corrected.	Deviation from 50 per cent.
c. c.	Per cent.						
0.5	3.41	+0.0438	+0.0381	+0.0819	-0.0001	+0.0818	-0.0087
1.0	6.83	.0341	.0503	.0844	-0.0003	.0841	-0.0064
1.5	10.24	.0284	.0547	.0831	-0.0004	.0827	-0.0078
2.11	14.40	.0233	.0616	.0849	-0.0005	.0844	-0.0061
2.5	17.06	.0206	.0650	.0856	-0.0006	.0850	-0.0055
3	20.48	.0177	.0692	.0860	-0.0008	.0861	-0.0044
3.5	23.89	.0151	.0727	.0878	-0.0009	.0869	-0.0036
4	27.30	.0128	.0759	.0887	-0.0010	.0877	-0.0028
4.5	30.72	.0106	.0789	.0895	-0.0012	.0883	-0.0022
5	34.13	.0086	.0814	.0900	-0.0013	.0887	-0.0018
6	40.96	+0.0048	.0864	.0912	-0.0015	.0897	-0.0008
7	47.78	+0.0012	.0910	.0922	-0.0018	.0904
8	54.61	-0.0024	.0951	.0927	-0.0020	.0907
9	61.44	-0.0061	.0995	.0934	-0.0023	.0911
10	68.26	-0.0100	.1041	.0941	-0.0026	.0915
11	75.09	-0.0144	.1090	.0946	-0.0028	.0918
12	81.91	-0.0197	.1147	.0950	-0.0031	.0919
13	88.74	-0.0270	.1227	.0957	-0.0034	.0923
14	95.57	-0.0401	.1363	.0962	-0.0036	.0926
14.65	100					

TABLE XXIV.—Titration of reduced trisulphonate (No. 7) with ferricyanide in buffer No. 7. (pH=3.91.)

K ₂ FeCy ₆	Reduction.	RT 2F ln $\frac{[S_2]}{[S_0]}$	E _h .	E'.	Acid correction.	E' corrected.	Deviation from 50 per cent.
c. c.	Per cent.						
0.5	3.34	+0.0440	+0.0354	+0.0794	-0.0001	+0.0793	-0.0098
1.0	6.67	.0345	.0453	.0798	-0.0003	.0795	-0.0096
1.5	10.01	.0287	.0520	.0807	-0.0004	.0803	-0.0088
2.0	13.34	.0244	.0573	.0817	-0.0005	.0812	-0.0079
2.5	16.68	.0210	.0617	.0827	-0.0006	.0821	-0.0070
3.0	20.01	.0181	.0657	.0838	-0.0008	.0830	-0.0061
3.5	23.35	.0155	.0691	.0846	-0.0009	.0837	-0.0054
4.0	26.68	.0132	.0728	.0860	-0.0010	.0850	-0.0041
4.5	30.02	.0111	.0759	.0870	-0.0012	.0858	-0.0033
5	33.35	.0090	.0789	.0879	-0.0013	.0866	-0.0025
6	40.03	.0053	.0842	.0895	-0.0015	.0880	-0.0011
7	46.69	+0.0017	.0888	.0905	-0.0018	.0887	-0.0004
8	53.36	-0.0018	.0933	.0915	-0.0020	.0895
9	60.04	-0.0053	.0975	.0922	-0.0023	.0899
10	66.71	-0.0091	.1019	.0928	-0.0026	.0902
11	73.38	-0.0132	.1066	.0934	-0.0028	.0906
12	80.05	-0.0181	.1118	.0937	-0.0031	.0906
13	86.73	-0.0245	.1187	.0942	-0.0034	.0908
14	93.40	-0.0346	.1289	.0943	-0.0036	.0907
14.5	96.74	-0.0444	.1387	.0943	-0.0037	.0906
14.99	100.00					

In Figure 7 are the deviations for trisulphonate No. 7 (Table XXIV). If the method be correct, the deviations indicated by circles show a molecular ratio $\frac{\text{disulphonate}}{\text{trisulphonate}} = \text{about } \frac{15}{85}$. This is confirmed as follows:

It was found on attempting to work out the characteristics of a trisulphonate by using preparation No. 7 in the method of mixtures that various ratios of the reduced and oxidized solution gave no

constant E'_o value. In buffer No. 5, for instance, the data were as follows:

Reduct- ant.	Oxidant.	E_h	E'_o
c. c.	c. c.		
3	7	+0.1648	+0.1537
4	6	.1583	.1530
5	5	.1523	.1523
6	4	.1457	.1510
7	3	.1382	.1493

The variation of E'_o is orderly and greater than the experimental error.

But let us assume a *molecular* ratio $\frac{\text{disulphonate}}{\text{trisulphonate}} = \frac{15}{85}$. If this mixture is reduced and 4 c. c. are mixed with 6 c. c. of the unreduced mixture, the ratios at the start will be

$$\frac{\text{reduced disulphonate}}{\text{disulphonate}} = \frac{0.6}{0.9}; \quad \frac{\text{reduced trisulphonate}}{\text{trisulphonate}} = \frac{3.4}{5.1}$$

The two systems will now interact to a common potential. The problem is to find the resultant ratio of $\frac{\text{reduced trisulphonate}}{\text{trisulphonate}}$. The problem can not be accurately solved unless the relative relations of the two systems are known. We could assume them to be known from studies on other preparations, but to avoid this assumption we shall assume as a first approximation that the two systems are so far apart on the potential scale that the preponderant trisulphonate system swamps the disulphonate system, converting all the reduced disulphonate to the oxidized form. In doing so a portion of the trisulphonate must be reduced.

In the case given above, the 0.6 c. c. reduced disulphonate acts upon the trisulphonate, decreasing it to $5.1 - 0.6 = 4.5$, and hence increases the reduced trisulphonate to $3.4 + 0.6 = 4.0$. The corrected ratio is $\frac{\text{reduced tri}}{\text{oxidized tri}} = \frac{4.0}{4.5}$. In a similar manner we can approximate the other corrected ratios listed below.

Mixture used.		Trisulphonate corrected.		$\frac{RT}{2F} \ln \frac{[S_r]}{[S_o]}$	E_h	E'_o
Reduct- ant.	Oxidant.	Reduct- ant.	Oxidant.			
c. c.	c. c.	c. c.	c. c.			
3	7	3.0	5.5	-0.0079	+0.1648	+0.1569
4	6	4.0	4.5	-0.0015	.1583	.1568
5	5	5.0	3.5	+0.0047	.1523	.1570
6	4	6.0	2.5	+0.0114	.1457	.1571
7	3	7.0	1.5	+0.0201	.1382	(.1583)
Average.....						+0.1570
\bar{w}_h						-0.1693
E_o						0.3263

Allowing in the above approximation for the error at the higher state of reduction of the whole, there is substantial agreement among the corrected values of E'_o . The average E_o value, 0.3263, is now in substantial agreement with the 0.3269 (see p. 1688) obtained with another sample of buffer No. 5 and with the pure trisulphonate No. 23, indicating that the assumption of 15 per cent impurity of No. 7 is approximately correct.

By two independent routes we have arrived at agreement that sample No. 7 contains presumably disulphonate in the molecular ratio approximately $\frac{\text{trisulphonate}}{\text{disulphonate}} = \frac{85}{15}$.

If two or more systems are very far apart, their distinctive titration curves will be apparent and more useful than the deviation curves just described.

We do not claim a high degree of accuracy for the method nor a complete examination of sources of error which may have entered into our procedure, but it is suggestive to note that titrations of disulphonate No. 20 in buffers Nos. 7 and 13 where the acid corrections are different and the buffer systems are different gave almost identical deviations. (Compare Table XIII with Table XXV.)

TABLE XXV.—Reduced indigo disulphonate (No. 20) titrated with ferricyanide in buffer No. 13.

K_3FeCy_6	Oxidation.	$\frac{RT}{2F} \ln \frac{[S_1]}{[S_2]}$	E_h	Acid correction.	E'_o corrected.	Deviation from -0.0826.
c. c.	Per cent.					
0	0	-----	-0.166			
1	7.46	+0.0329	-0.1174	-0.0002	-0.0847	-0.0021
2	14.91	+0.0227	-0.1033	-0.0004	-0.0840	-0.0014
3	22.37	+0.0163	-0.0994	-0.0003	-0.0837	-0.0011
4	29.83	+0.0112	-0.0935	-0.0007	-0.0830	-0.0004
5	37.28	+0.0068	-0.0888	-0.0009	-0.0829	-0.0003
6	44.74	+0.0028	-0.0845	-0.0011	-0.0828	-0.0002
7	52.20	-0.0012	-0.0803	-0.0012	-0.0827	-0.0001
8	59.66	-0.0051	-0.0761	-0.0014	-0.0825	.0000
9	67.11	-0.0093	-0.0718	-0.0016	-0.0827	-0.0001
10	74.56	-0.0141	-0.0668	-0.0017	-0.0826	.0000
11	82.02	-0.0198	-0.0609	-0.0019	-0.0826	.0000
12	89.48	-0.0280	-0.0527	-0.0020	-0.0827	-0.0001
13	96.95	-0.0452	-0.0390	-0.0022	-0.0834	-0.0008
13.41	100.00	-----	+0.01			

It has been the custom to employ electrode measurements in estimating the end point of a titration. This emphasis of the end of a titration curve and the neglect of the complete curve is unfortunate in several respects. In the first place, the complete curve can furnish information which no end-point titration can. In the second place, analysis by end-point titration involves errors of weighing samples, standardizing solutions, and estimation of moisture in the sample used. None of these sources of error is involved

in the method we have outlined. The errors are of quite different nature and can easily be avoided if the subject be given further study.

We shall now return for a moment to a question which has already been answered by the data given in previous sections. Is it possible that our "trisulphonate" is a fortuitous mixture of disulphonate and tetrasulphonate, yielding an analysis of a hypothetical

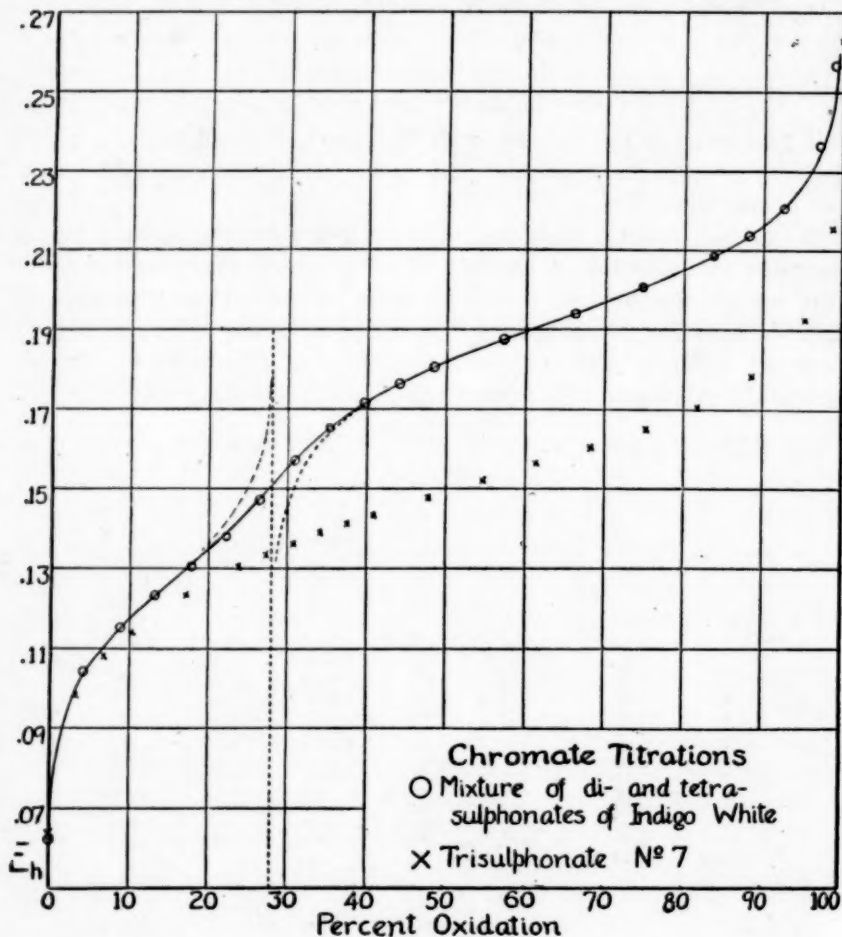


FIG. 8.

trisulphonate? We have already shown that trisulphonate No. 23 acts like a homogeneous substance. What would be found were the trisulphonate a mixture of the di- and tetra-sulphonates is clearly revealed in Figure 8. The theoretical titration curves of the di- and tetra-sulphonates are represented in isolation by means of the type curves and are scaled to correspond to the percentages employed. The experimental data, represented by the centers of the circles,

clearly follow the resultant of the two type curves. The titration of the impure trisulphonate No. 7 at the same pH is shown below by crosses, the positions of which are comparatively close to those which would have been found had the pure sample been used. The significance of Figure 8 is evident.

Summary.

A brief review of the literature reveals not only conflicting statements regarding the conduct of indigo and its sulphonates *in vitro* and *in vivo* but also a lack of appreciation of certain theoretical aspects which could have been known only through a quantitative study of oxidation-reduction equilibria. This paper furnishes that study.

Pure samples of the mono-, di-, tri-, and tetra-sulphonates of indigo have been prepared.

With these samples there have been found, by the methods described in this and previous papers, the characteristic electrode potentials at 30°.

A rational equation which fits the experimental facts is the following:

$$E_h = E_o - \frac{RT}{nF} \ln \frac{[S_r]}{[S_o]} + \frac{RT}{nF} \ln [K_1[H^+] + [H^+]^2]$$

Here E_h is the observed electrode potential referred to the hydrogen standard, $[S_r]$ and $[S_o]$ are the concentrations of total reductant and total oxidant, $[H^+]$ is the hydron concentration of the solution, and K_1 is the acid dissociation constant of one of the two hydrogens of the hydrogenated leuco-compound (the dissociation of the sulphonic acids is not considered).

The number, n , of electrons concerned in the reversible oxidation-reduction is 2.

The second acidic hydrogen of the leuco-compound is shown to have a dissociation constant less than 10^{-12} .

The values of E_o and K_1 are tabulated below.

System.	E_o .	K_1 .
Monosulphonate of indigo \rightleftharpoons leuco compound	+0.262	1.6×10^{-3}
Disulphonate of indigo \rightleftharpoons leuco compound	+0.291	4.9×10^{-3}
Trisulphonate of indigo \rightleftharpoons leuco compound	+0.332	7.7×10^{-3}
Tetrasulphonate of indigo \rightleftharpoons leuco compound	+0.365	11.2×10^{-3}

The system indigo \rightleftharpoons indigo-white is not adapted to accurate experimental study in aqueous solution. Very rough measurements suggest $K_1 = 10^{-8}$ and E_o near that of the monosulphonate.

The influence of substitution is shown in the above table, confirming in more detail the data of 1921, which showed that electrode measurements furnish a means of studying the effect of substitution.

Anomalies with borate buffers are shown, and a suggestion of a "salt effect" is obtained with other buffer systems.

The acidic nature of the leuco-compounds and the ionization of but one hydrogen at moderate alkalinities are independently treated.

An electrometric method for analysis of mixtures of the sulphonates has been devised.

The data furnish the information necessary wherever the reversible oxidation-reduction of an indigo sulphonate is applied, and, in particular, establish the characteristics of the sulphonates of indigo for use in the colorimetric estimation of oxidation-reduction intensities of biological solutions.

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COURT DECISIONS PERTAINING TO VENEREAL DISEASES.

COURT UPHOLDS DETENTION OF PERSON SUSPECTED OF BEING VENEREALLY INFECTED.

A woman who had been arrested and charged with conducting a house of ill fame was detained under instructions from the health department of the city of Los Angeles not to release her until she had submitted to an examination to determine whether she was venereally infected. She sought her release by habeas corpus proceedings. The health department had been furnished information warranting the conclusion that the woman conducted a house of ill fame, that she was an inmate thereof, and that she personally participated in the unlawful acts carried on therein.

The California District Court of Appeals, second district, division 1, held ¹ that this information furnished reasonable ground to believe that the woman was venereally infected, and that this was all that was necessary to authorize the health department to enforce quarantine measures against her.

¹ Ex parte Clemente, 215 Pac. 698.

VENEREAL DISEASE ORDINANCE CONSTRUED.

One of the sections of the venereal disease ordinance of Wichita, Kans., provided that an infected person, not a prostitute, "may be released" from isolation or quarantine upon giving a bond or cash guaranty, the application for release being made to the city physician. The Supreme Court of Kansas has decided ¹ that the section in question does not compel the release of a person but authorizes it if in the judgment of the city physician the public welfare will not suffer thereby.

DEATHS DURING WEEK ENDED JULY 14, 1923.

Summary of information received by telegraph from industrial insurance companies for week ended July 14, 1923, and corresponding week of 1922. (From the Weekly Health Index, July 17, 1923, issued by the Bureau of the Census, Department of Commerce.)

	Week ended July 14, 1923.	Corresponding week, 1922.
Policies in force.....	54, 126, 849	49, 659, 725
Number of death claims.....	9, 369	8, 616
Death claims per 1,000 policies in force, annual rate.....	9.0	9.0

Deaths from all causes in certain large cities of the United States during the week ended July 14, 1923, infant mortality, annual death rate, and comparison with corresponding week of 1922. (From the Weekly Health Index, July 17, 1923, issued by the Bureau of the Census, Department of Commerce.)

	Week ended July 14, 1923.		Annual death rate per 1,000, corre- sponding week, 1922.	Deaths under 1 year.		Infant mortality rate, week ended July 14, 1923. ^b
	Total deaths.	Death rate. ^a		Week ended July 14, 1923.	Corre- sponding week, 1922.	
Total.....	6, 129	10.9	10.8	733	828
Akron, Ohio.....	21	5.3	6.3	4	1	47
Albany, N. Y. ^c	32	14.2	9.0	4	5	88
Atlanta, Ga.....	96	22.5	16.1	21	9
Baltimore, Md. ^c	176	11.9	13.1	17	37	50
Birmingham, Ala.....	63	16.8	15.3	4	5
Boston, Mass.....	164	11.1	12.2	23	25	66
Bridgeport, Conn.....	28	10.2	8.4	2	5	28
Buffalo, N. Y.....	109	10.6	12.2	17	21	71
Cambridge, Mass.....	23	10.8	10.3	1	1	18
Camden, N. J. ^c	37	15.5	6.0	5	3	83
Chicago, Ill.....	509	9.2	9.1	52	61
Cincinnati, Ohio.....	111	14.2	12.0	9	4	59
Cleveland, Ohio.....	165	9.7	8.7	23	22	63
Columbus, Ohio.....	70	14.0	12.5	3	8	31
Dallas, Tex.....	39	11.5	11.2	6	11
Dayton, Ohio.....	31	9.8	11.3	4	6	66
Denver, Colo.....	68	13.0	9.9	8	4
Des Moines, Iowa.....	19	7.0	4	4
Detroit, Mich.....	192	10.1	10.3	31	41	62
Duluth, Minn.....	13	6.4	0	0
Erie, Pa.....	24	11.1	7.1	2	0	41
Fall River, Mass. ^c	25	10.8	9.9	4	5	57
Flint, Mich.....	17	7.5	2	40

^a Annual rate per 1,000 population.

^b Deaths under 1 year per 1,000 births—an annual rate based on deaths under 1 year for the week and estimated births for 1922. Cities left blank are not in the registration area for births.

^c Deaths for week ended Friday, July 13, 1923.

¹ Ex parte Irby, 215 Pac. 449; Ex parte Hollowell, 215 Pac. 450.

Deaths from all causes in certain large cities of the United States during the week ended July 14, 1923, infant mortality, annual death rate, and comparison with corresponding week of 1922. (From the Weekly Health Index, July 17, 1923, issued by the Bureau of the Census, Department of Commerce.)—Continued.

City.	Week ended July 14, 1923.		Annual death rate per 1,000, corre- sponding week, 1922.	Deaths under 1 year.		Infant mor- tality rate, week ended July 14, 1923.
	Total deaths.	Death rate.		Week ended July 14, 1923.	Corre- sponding week, 1922.	
Fort Worth, Tex.	24	8.7	11.4	1	4
Grand Rapids, Mich.	25	8.9	12.0	1	3	16
Houston, Tex.	36	12.1	11.5	4	7
Indianapolis, Ind.	71	10.8	12.3	7	8	54
Jacksonville, Fla.	23	12.0	14.4	5	1
Jersey City, N. J.	61	10.3	12.4	15	19	101
Kansas City, Kans.	21	9.5	8.7	0	1	0
Kansas City, Mo.	31	13.8	12.4	17	10
Los Angeles, Calif.	200	16.3	14.5	25	12	94
Louisville, Ky.	76	15.4	16.0	23	9	248
Lynn, Mass.	17	7.7	11.8	2	5	35
Lynn, Mass.	14	7.1	2	53
Memphis, Tenn.	61	18.7	10.9	10	3
Milwaukee, Wis.	67	7.2	7.7	14	19	70
Minneapolis, Minn.	98	12.5	9.0	11	5	60
Nashville, Tenn.	43	18.5	16.5	8	7
New Bedford, Mass.	21	8.4	11.0	3	7	47
New Haven, Conn.	29	8.7	10.1	4	5	52
New Orleans, La.	134	17.3	16.7	14	21
New York, N. Y.	1,683	9.5	9.8	114	158	46
Bronx borough.	123	7.6	7.3	6	11	21
Brooklyn borough.	346	8.4	8.9	39	62	41
Manhattan borough.	489	11.2	11.2	60	71	58
Queens borough.	97	9.4	9.0	7	9	37
Richmond borough.	28	11.4	18.0	2	5	36
Newark, N. J.	66	7.8	9.3	11	19	52
Norfolk, Va.	27	8.8	10.0	10	6	176
Oakland, Calif.	42	9.2	9.6	5
Omaha, Nebr.	39	9.9	10.9	1	3	11
Paterson, N. J.	33	12.3	9.0	2	4	32
Philadelphia, Pa.	388	10.5	10.4	40	57	52
Pittsburgh, Pa.	128	10.9	12.6	20	21	70
Portland, Oreg.	52	9.9	8.5	4	7	40
Providence, R. I.	61	13.1	10.4	13	9	106
Richmond, Va.	57	16.4	12.6	15	10	184
Rochester, N. Y.	50	8.2	11.0	7	8	55
St. Louis, Mo.	108	12.8	9.6	15	10
St. Paul, Minn.	54	11.6	9.6	3	7	28
Salt Lake City, Utah.	36	14.9	13.5	7	6	114
San Antonio, Tex.	60	16.9	14.6	12	15
San Francisco, Calif.	123	11.9	13.5	5	8	30
Seattle, Wash.	50	8.3	9.9	4	8	35
Spokane, Wash.	25	12.5	12.5	4	1	87
Springfield, Mass.	22	8.0	8.6	2	1	29
Syracuse, N. Y.	47	13.3	16.7	5	11	65
Tacoma, Wash.	19	9.7	0	0
Toledo, Ohio.	59	11.5	13.8	7	5	71
Trenton, N. J.	31	12.7	12.9	4	2	68
Utica, N. Y.	16	8.1	4	0
Washington, D. C.	112	13.3	12.3	6	11	34
Wilmington, Del.	18	8.0	10.4	0	2	0
Worcester, Mass.	36	9.8	10.8	7	7	80
Yonkers, N. Y.	17	8.2	9.9	0	2	0
Youngstown, Ohio.	25	9.8	11.4	3	5	41

• Deaths for week ended Friday, July 13, 1923.

PREVALENCE OF DISEASE.

No health department, State or local, can effectively prevent or control disease without knowledge of when, where, and under what conditions cases are occurring.

UNITED STATES.

CURRENT STATE SUMMARIES.

These reports are preliminary, and the figures are subject to change when later returns are received by the State health officers.

Reports for Week Ended July 21, 1923.

ARIZONA.		CONNECTICUT.	
	Cases.		Cases.
Chicken pox.....	1	Cerebrospinal meningitis.....	4
Diphtheria.....	2	Chicken pox.....	21
Measles.....	1	Conjunctivitis.....	1
Mumps.....	1	Diphtheria.....	27
Poliomyelitis.....	1	Dysentery (bacillary).....	3
Scarlet fever.....	1	Lethargic encephalitis.....	3
Tuberculosis.....	20	Malaria.....	7
Typhoid fever.....	1	Measles.....	73
Whooping cough.....	5	Mumps.....	8
		Pneumonia (lobar).....	8
		Poliomyelitis.....	3
		Scarlet fever.....	23
		Septic sore throat.....	1
		Tuberculosis (all forms).....	41
		Typhoid fever.....	9
		Whooping cough.....	63
ARKANSAS.		FLORIDA.	
Cerebrospinal meningitis.....	1	Dengue.....	1
Chicken pox.....	11	Diphtheria.....	4
Hookworm disease.....	2	Influenza.....	1
Influenza.....	3	Malaria.....	7
Malaria.....	108	Scarlet fever.....	1
Measles.....	61	Typhoid fever.....	5
Paratyphoid fever.....	6		
Pellagra.....	15		
Poliomyelitis.....	1		
Smallpox.....	3		
Trachoma.....	2		
Tuberculosis.....	7		
Typhoid fever.....	38		
Whooping cough.....	11		
		GEORGIA.	
		Chicken pox.....	3
		Dengue.....	1
		Diphtheria.....	9
		Dysentery (bacillary).....	1
		Hookworm disease.....	18
		Influenza.....	3
		Malaria.....	47
		Measles.....	92
		Mumps.....	1
		Pneumonia.....	3
		Scarlet fever.....	3
		Smallpox.....	15
COLORADO.			
(Exclusive of Denver.)			
Chicken pox.....	4		
Diphtheria.....	13		
Measles.....	37		
Mumps.....	3		
Scarlet fever.....	6		
Smallpox.....	1		
Tuberculosis.....	123		
Typhoid fever.....	8		
Whooping cough.....	2		

Reports for Week Ended July 21, 1923—Continued.

GEORGIA—continued.		MARYLAND. ¹	
	Cases.		Cases.
Tuberculosis (pulmonary).....	17	Anthrax.....	1
Typhoid fever.....	42	Chicken pox.....	13
Whooping cough.....	25	Diphtheria.....	20
ILLINOIS.		Dysentery.....	9
Cerebrospinal meningitis:		Influenza.....	2
Carroll County.....	1	Lethargic encephalitis.....	2
Chicago.....	1	Malaria.....	13
Richland County.....	1	Measles.....	144
Diphtheria:		Mumps.....	10
Cook County (including Chicago).....	66	Paratyphoid fever.....	2
Chicago.....	61	Pneumonia (all forms).....	22
Scattering.....	34	Scarlet fever.....	22
Influenza.....	5	Septic sore throat.....	1
Lethargic encephalitis:		Tuberculosis.....	80
Chicago.....	1	Typhoid fever.....	25
Kane County.....	1	Whooping cough.....	87
Pneumonia.....	98	MASSACHUSETTS.	
Poliomyelitis:		Anthrax.....	1
Chicago.....	1	Cerebrospinal meningitis.....	5
Jackson County.....	1	Chicken pox.....	96
McLean County.....	1	Conjunctivitis (suppurative).....	13
Sangamon County.....	1	Diphtheria.....	95
Whiteside County.....	1	German measles.....	7
Scarlet fever:		Hookworm disease.....	1
Cook County (including Chicago).....	24	Influenza.....	1
Chicago.....	23	Lethargic encephalitis.....	2
Scattering.....	19	Malaria.....	1
Smallpox.....	10	Measles.....	236
Typhoid fever.....	27	Mumps.....	51
Whooping cough.....	254	Ophthalmia neonatorum.....	17
IOWA.		Pellagra.....	1
Diphtheria.....	22	Pneumonia (lobar).....	25
Scarlet fever.....	25	Poliomyelitis.....	2
Smallpox.....	6	Scarlet fever.....	102
Typhoid fever.....	2	Septic sore throat.....	2
KANSAS.		Tetanus.....	2
Chicken pox.....	14	Trachoma.....	4
Diphtheria.....	17	Tuberculosis (all forms).....	142
Measles.....	115	Typhoid fever.....	17
Mumps.....	8	Whooping cough.....	114
Pneumonia.....	3	MICHIGAN.	
Poliomyelitis.....	1	Diphtheria.....	90
Scarlet fever.....	33	Measles.....	389
Smallpox.....	6	Pneumonia.....	57
Tuberculosis.....	31	Scarlet fever.....	123
Typhoid fever.....	23	Smallpox.....	47
Whooping cough.....	105	Tuberculosis.....	56
LOUISIANA.		Typhoid fever.....	22
Dengue.....	8	Whooping cough.....	230
Malaria.....	36	MONTANA.	
Smallpox.....	3	Diphtheria.....	2
Typhoid fever.....	19	Rocky Mountain spotted fever—Jordan.....	1
Whooping cough.....	12	Smallpox.....	10
MAINE.		Typhoid fever.....	2
Chicken pox.....	11	NEW JERSEY.	
Diphtheria.....	5	Cerebrospinal meningitis.....	2
Measles.....	103	Chicken pox.....	48
Pneumonia.....	5	Diphtheria.....	68
Scarlet fever.....	7	Dysentery.....	3
Tuberculosis.....	4	Influenza.....	3
Typhoid fever.....	4		
Whooping cough.....	4		

¹ Week ended Friday.

Reports for Week Ended July 21, 1923—Continued.

NEW JERSEY—continued.		TEXAS—continued.	
	Cases.		Cases.
Malaria.....	1	Poliomyelitis.....	1
Measles.....	148	Scarlet fever.....	10
Pneumonia.....	31	Smallpox.....	1
Poliomyelitis.....	2	Tuberculosis.....	24
Scarlet fever.....	23	Typhoid fever.....	28
Smallpox.....	1	Whooping cough.....	58
Typhoid fever.....	16		
Whooping cough.....	102		
NEW MEXICO.		VERMONT.	
Diphtheria.....	11	Chicken pox.....	6
Measles.....	12	Measles.....	43
Pneumonia.....	1	Mumps.....	8
Tuberculosis.....	11	Scarlet fever.....	9
Typhoid fever.....	2	Smallpox.....	8
Whooping cough.....	2	Whooping cough.....	24
NORTH CAROLINA.		WASHINGTON.	
Cerebrospinal meningitis.....	2	Chicken pox.....	16
Chicken pox.....	12	Diphtheria:	
Diphtheria.....	29	Spokane.....	9
German measles.....	2	Scattering.....	22
Measles.....	328	Impetigo contagiosa.....	1
Poliomyelitis.....	1	Measles:	
Scarlet fever.....	14	Seattle.....	12
Septic sore throat.....	2	Scattering.....	30
Smallpox.....	22	Mumps.....	7
Trachoma.....	1	Poliomyelitis—Seattle.....	2
Typhoid fever.....	112	Scarlet fever.....	24
Whooping cough.....	283	Smallpox.....	18
		Tuberculosis.....	30
OREGON.		Typhoid fever.....	4
		Whooping cough.....	80
Chicken pox.....	4		
Diphtheria.....	11		
Measles.....	6		
Mumps.....	1		
Pneumonia.....	13		
Scarlet fever.....	5		
Smallpox.....	11		
Tuberculosis.....	7		
Whooping cough.....	2		
SOUTH DAKOTA.			
Chicken pox.....	4		
Diphtheria.....	8		
Measles.....	12		
Scarlet fever.....	13		
Tuberculosis.....	7		
Whooping cough.....	3		
TEXAS.			
Dengue.....	1		
Diphtheria.....	11		
Influenza.....	8		
Measles.....	18		
Mumps.....	4		
Paratyphoid fever.....	1		
Pneumonia.....	3		

¹ Deaths.

Reports for Week Ended July 14, 1923.

DISTRICT OF COLUMBIA.		NEBRASKA—continued.	
	Cases.		Cases.
Cerebrospinal meningitis.....	1	Scarlet fever.....	6
Chicken pox.....	5	Typhoid fever.....	22
Diphtheria.....	2	Whooping cough.....	15
Lethargic encephalitis.....	1		
Measles.....	14	NORTH DAKOTA.	
Scarlet fever.....	6	Chicken pox.....	14
Tuberculosis.....	27	Measles.....	47
Typhoid fever.....	6	Pneumonia.....	2
Whooping cough.....	22	Scarlet fever.....	8
		Smallpox.....	5
NEBRASKA.		Trachoma.....	2
Chicken pox.....	2	Tuberculosis.....	1
Measles.....	8	Whooping cough.....	2
Mumps.....	4		

SUMMARY OF CASES REPORTED MONTHLY BY STATES.

The following summary of monthly State reports is published weekly and covers only those States from which reports are received during the current week:

State.	Cerebrospinal meningitis.	Diphtheria.	Influenza.	Malaria.	Measles.	Pellagra.	Pollomyelitis.	Scarlet fever.	Smallpox.	Typhoid fever.
<i>June, 1923.</i>										
Alabama.....		28	115	465	1,680	135	1	26	45	216
Indiana.....	13	129	2		3,895		3	199	236	33
Louisiana.....	4	42	62	116	628	30	4	5	20	110
Minnesota.....		169			1,272		5	432	88	29
New York.....	15	1,069	65	12	12,246		24	1,539	15	126
Rhode Island.....		55			167			35		2
Washington.....	2	88			352			112	113	26

RECIPROCAL NOTIFICATION, JUNE, 1923.

Cases of communicable diseases referred during June, 1923, to other State health departments by departments of health of certain States.

Referred by—	Diphtheria.	Measles.	Pollomyelitis.	Scarlet fever.	Smallpox.	Trachoma.	Tuberculosis.	Typhoid fever.
Connecticut.....	1	1						
Illinois.....						1	15	
Louisiana.....								2
Massachusetts.....	1							
Minnesota.....		1					48	
New Jersey.....				1				1
New York.....	1	2	1		1			2

CITY REPORTS FOR WEEK ENDED JULY 7, 1923.

CEREBROSPINAL MENINGITIS.

The column headed "Median for previous years" gives the median number of cases reported during the corresponding week of the years 1915 to 1922, inclusive. In instances in which data for the full eight years are incomplete, the median is that for the number of years for which information is available.

City.	Median for previous years.	Week ended July 7, 1923.		City.	Median for previous years.	Week ended July 7, 1923.	
		Cases.	Deaths.			Cases.	Deaths.
California:				Minnesota:			
Bakersfield.....	0		1	Winona.....			1
Los Angeles.....	0	2		Missouri:			
Sacramento.....	0	1		St. Louis.....	1	1	
San Francisco.....	1		1	New York:			
Connecticut:				New York.....	6	1	2
New London.....	0	1	1	Ohio:			
Waterbury.....	0	1	1	Cleveland.....	0	1	1
Illinois:				Pennsylvania:			
Chicago.....	1	2		Farrell.....	0	1	
Rockford.....	0		1	Philadelphia.....	0	1	
Kentucky:				Pittsburgh.....	0	1	
Louisville.....	1	1		Texas:			
Louisiana:				Beaumont.....	0	1	
New Orleans.....	0	1	1	West Virginia:			
Massachusetts:				Huntington.....	0		1
Lynn.....	0	1		Wisconsin:			
				Milwaukee.....	0	3	3

DIPHTHERIA.

See p. 1731; also Current State summaries, p. 1721, and Monthly summaries by States, p. 1724.

INFLUENZA.

City.	Cases.		Deaths, week ended July 7, 1923.	City.	Cases.		Deaths, week ended July 7, 1923.
	Week ended July 8, 1922.	Week ended July 7, 1923.			Week ended July 8, 1922.	Week ended July 7, 1923.	
Alabama:				Massachusetts—Contd.			
Montgomery.....		1		Quincy.....	1		
Tuscaloosa.....		1		Worcester.....	1		
California:				Missouri:			
Long Beach.....			1	Kansas City.....		1	1
Los Angeles.....	3		1	New Jersey:			
Oakland.....			1	Trenton.....	1		
San Francisco.....		4	1	New York:			
Stockton.....		1		Buffalo.....			2
Colorado:				New York.....	1	1	2
Denver.....			1	Syracuse.....			1
District of Columbia:				Ohio:			
Washington.....	1			Cleveland.....			2
Georgia:				Pennsylvania:			
Atlanta.....		2		Philadelphia.....		1	
Illinois:				Pittsburgh.....			1
Chicago.....	1	4		Texas:			
Maine:				Dallas.....			1
Portland.....			1	San Antonio.....			1
Massachusetts:				Virginia:			
Holyoke.....	1			Richmond.....			1

LEPROSY.

City.	Cases.	Deaths.
California:		
Los Angeles.....	1	

CITY REPORTS FOR WEEK ENDED JULY 7, 1923—Continued.

LETHARGIC ENCEPHALITIS.

City.	Cases.	Deaths.
California:		
San Francisco.....		1

MALARIA.

City.	Cases.	Deaths.	City.	Cases.	Deaths.
Alabama:			Kentucky:		
Birmingham.....	2		Owensboro.....	1	
Mobile.....	1		New Jersey:		
Montgomery.....	1		New Jersey.....		
Arkansas:			East Orange.....	1	
Little Rock.....	1		Newark.....	3	
Georgia:			New York:		
Atlanta.....	1		New York.....	1	
Augusta.....	1		Ohio:		
Brunswick.....	6		Lorain.....	1	
Rome.....	1		Tennessee:		
Iowa:			Memphis.....	10	
Dubuque.....	1		Texas:		
			Houston.....		1

MEASLES.

See p. 1731; also Current State summaries, p. 1721, and Monthly summaries by States, p. 1724.

PELLAGRA.

City.	Cases.	Deaths.	City.	Cases.	Deaths.
Alabama:			Tennessee:		
Tuscaloosa.....	5		Memphis.....	1	2
Georgia:			Nashville.....		1
Atlanta.....	1	1	Texas:		
Savannah.....	1	1	Dallas.....		1
North Carolina:			El Paso.....		1
Greensboro.....		1	Galveston.....	1	1
South Carolina:			San Antonio.....		1
Columbia.....		2	West Virginia:		
			Huntington.....		1

PNEUMONIA (ALL FORMS).

City.	Cases.	Deaths.	City.	Cases.	Deaths.
Alabama:			Georgia:		
Birmingham.....	9	4	Atlanta.....	16	8
Montgomery.....		2	Augusta.....		2
California:			Savannah.....		3
Alameda.....	1		Illinois:		
Eureka.....		1	Bloomington.....		1
Long Beach.....		1	Chicago.....	73	31
Los Angeles.....	21	12	Cicero.....	2	1
Oakland.....		1	Elgin.....	2	
Riverside.....		1	Freeport.....		2
Sacramento.....	3	2	Galesburg.....		1
San Bernardino.....		2	Oak Park.....		2
San Diego.....	6	5	Rockford.....		2
San Francisco.....		6	Springfield.....		1
San Jose.....		1	Indiana:		
Santa Ana.....		1	Anderson.....		1
Santa Barbara.....		1	East Chicago.....		1
Stockton.....	1		Indianapolis.....		8
Colorado:			Kokomo.....		1
Denver.....		1	La Fayette.....		1
Connecticut:			Logansport.....		1
Bridgeport.....	1		Muncie.....		1
New Haven.....	2	1	South Bend.....		1
District of Columbia:			Kansas:		
Washington.....		11	Hutchinson.....	1	
			Kansas City.....	1	

CITY REPORTS FOR WEEK ENDED JULY 7, 1923—Continued.

PNEUMONIA (ALL FORMS)—Continued.

City.	Cases.	Deaths.	City.	Cases.	Deaths.
Kentucky:			New York:		
Covington.....		1	Albany.....	4	1
Louisville.....		4	Amsterdam.....		1
Louisiana:			Buffalo.....	5	2
New Orleans.....	11	8	Lackawanna.....	4	1
Maine:			Lockport.....		1
Lewiston.....		1	Mount Vernon.....		1
Portland.....		2	New York.....	95	63
Maryland:			Olean.....		1
Baltimore.....		14	Rochester.....		2
Massachusetts:			Schenectady.....		4
Boston.....		7	Syracuse.....	9	3
Brockton.....		1	Watertown.....		1
Cambridge.....		1	Yonkers.....		1
Chelsea.....	1		North Carolina:		
Clinton.....		1	Greensboro.....		1
Fall River.....	3	2	Raleigh.....		1
Haverhill.....		1	Wilmington.....		1
Holyoke.....		2	Ohio:		
Lawrence.....		1	Cincinnati.....		10
Leominster.....	1		Cleveland.....		14
Lowell.....		3	Columbus.....		5
Malden.....	1		Dayton.....	1	
Melrose.....		1	Mansfield.....	1	
New Bedford.....		1	Springfield.....		2
Newton.....		1	Toledo.....		3
North Adams.....		1	Youngstown.....		1
Pittsfield.....		1	Oklahoma:		
Quincy.....		1	Oklahoma.....		3
Wakefield.....	1		Oregon:		
Watertown.....		1	Portland.....		3
Woburn.....		1	Pennsylvania:		
Worcester.....		1	Philadelphia.....	30	22
Michigan:			Pittsburgh.....		12
Penton Harbor.....	1		Rhode Island:		
Flint.....		3	Cranston.....	1	
Highland Park.....		1	Providence.....		1
Kalamazoo.....		2	South Carolina:		
Minnesota:			Charleston.....		2
Minneapolis.....		2	Columbia.....		3
St. Paul.....		3	Tennessee:		
Missouri:			Memphis.....		10
Kansas City.....		3	Nashville.....		2
St. Joseph.....		1	Texas:		
Springfield.....		4	Dallas.....		1
Montana:			El Paso.....		3
Billings.....		1	Fort Worth.....		1
Missoula.....	1		Galveston.....		1
Nebraska:			Houston.....		1
Omaha.....		6	San Antonio.....		3
New Hampshire:			Utah:		
Concord.....		1	Provo.....	3	1
Keene.....		1	Salt Lake City.....		1
New Jersey:			Vermont:		
Atlantic City.....	1		Burlington.....		2
Hoboken.....		1	Virginia:		
Jersey City.....	1		Norfolk.....		1
Morristown.....	3	1	Richmond.....		3
Newark.....	8	5	Wisconsin:		
Passaic.....	1		Racine.....		1
Paterson.....	1		Superior.....		1
Plainfield.....	1				
Trenton.....	2	2			
West Hoboken.....		1			
West Orange.....	1				

CITY REPORTS FOR WEEK ENDED JULY 7, 1923—Continued.

POLIOMYELITIS (INFANTILE PARALYSIS).

The column headed "Median for previous years" gives the median number of cases reported during the corresponding week of the years 1915 to 1922, inclusive. In instances in which data for the full eight years are incomplete, the median is that for the number of years for which information is available.

City.	Median for pre- vious years.	Week ended July 7, 1923.		City.	Median for pre- vious years.	Week ended July 7, 1923.	
		Cases.	Deaths.			Cases.	Deaths.
Connecticut:				New York:			
New London.....	0	1	New York.....	4	7
Iowa:				Oklahoma:			
Cedar Rapids.....	0	1	Oklahoma.....	0	1
Kentucky:				Tulsa.....	0	1
Louisville.....	0	1	Virginia:			
New Jersey:				Richmond.....	0	1
Newark.....	0	1				

RABIES IN ANIMALS.

City.	Cases.	City.	Cases.
California:		Ohio:	
Los Angeles.....	8	Columbus.....	1
Kentucky:		Texas:	
Owensboro.....	1	Dallas.....	1
Missouri:			
Kansas City.....	2		

SCARLET FEVER.

See p. 1731; also Current State summaries, p. 1721, and Monthly summaries by States, p. 1724.

CITY REPORTS FOR WEEK ENDED JULY 7, 1923—Continued.

SMALLPOX.

The column headed "Median for previous years" gives the median number of cases reported during the corresponding week of the years 1915 to 1922, inclusive. In instances in which data for the full eight years are incomplete, the median is that for the number of years for which information is available.

City.	Median for pre- vious years.	Week ended July 7, 1923.		City.	Median for pre- vious years.	Week ended July 7, 1923.	
		Cases.	Deaths.			Cases.	Deaths.
California:				North Carolina:			
Long Beach.....	0	1	Durham.....	0	2
Los Angeles.....	1	3	Raleigh.....	0	1
Oakland.....	0	1	Winston-Salem.....	0	3
Georgia:				North Dakota:			
Atlanta.....	5	8	Grand Forks.....	2	1
Savannah.....	0	1	Ohio:			
Illinois:				Cleveland.....	0	1
Chicago.....	0	7	Norwood.....	0	1
Indiana:				Sandusky.....	0	2
Anderson.....	0	1	Toledo.....	1	1
Gary.....	0	2	Oklahoma:			
Indianapolis.....	0	1	Oklahoma.....	2	3
Mishawaka.....	0	2	Tulsa.....	0	3
Muncie.....	0	2	Oregon:			
Iowa:				Portland.....	3	11
Cedar Rapids.....	0	1	Pennsylvania:			
Des Moines.....	3	3	York.....	0	5
Kansas:				Tennessee:			
Wichita.....	3	2	Chattanooga.....	0	4
Michigan:				Knoxville.....	0	10
Highland Park.....	0	1	Texas:			
Minnesota:				Houston.....	0	1
Minneapolis.....	6	3	San Antonio.....	1	1
St. Paul.....	0	2	Vermont:			
Winona.....	0	1	Burlington.....	0	2
Montana:				Washington:			
Billings.....	0	1	Seattle.....	1	7
Great Falls.....	0	3	Spokane.....	4	1
Missoula.....	0	1	Vancouver.....	0	1
New Jersey:				Wisconsin:			
Trenton.....	0	2	Kenosha.....	0	2
New York:				Milwaukee.....	3	1
Buffalo.....	0	1	Superior.....	1	3
Niagara Falls.....	0	3				

TETANUS.

City.	Cases.	Deaths.	City.	Cases.	Deaths.
Alabama:			New Jersey:		
Birmingham.....	1	1	Morristown.....	1
Illinois:			Newark.....	1
Chicago.....	2	1	New York:		
Elgin.....	1	1	Lackawanna.....	1
Indiana:			New York.....	1
Michigan City.....	1	1	Schenectady.....	1
Kentucky:			Ohio:		
Owensboro.....	1	Cleveland.....	1
Massachusetts:			Pennsylvania:		
North Adams.....	1	Pittsburgh.....	1
Missouri:					
St. Joseph.....	2			
Springfield.....	1			

CITY REPORTS FOR WEEK ENDED JULY 7, 1923—Continued.

TUBERCULOSIS.

See p. 1731; also Current State summaries, p. 1721.

TYPHOID FEVER.

The column headed "Median for previous years" gives the median number of cases reported during the corresponding week of the years 1915 to 1922, inclusive. In instances in which data for the full eight years are incomplete, the median is that for the number of years for which information is available.

City.	Median for previous years.	Week ended July 7, 1923.		City.	Median for previous years.	Week ended July 7, 1923.	
		Cases.	Deaths.			Cases.	Deaths.
Alabama:				New York:			
Birmingham.....	5	3	1	Albany.....	2	1
Montgomery.....	0	1	Auburn.....	0	1
Tuscaloosa.....	0	1	Buffalo.....	0	1
Arkansas:				New York.....	15	6	2
Little Rock.....	1	2	Rome.....	0	1
California:				Schenectady.....	0	1
Los Angeles.....	4	3	1	Syracuse.....	0	1
Pasadena.....	0	1	Troy.....	0	1
Sacramento.....	0	1	North Carolina:			
Colorado:				Greensboro.....	0	9	1
Pueblo.....	1	3	Wilmington.....	0	1
Connecticut:				Winston-Salem.....	5	2
Greenwich.....	0	1	Ohio:			
New Haven.....	1	1	Akron.....	0	1
Georgia:				Cincinnati.....	1	2	1
Atlanta.....	3	3	Columbus.....	3	1
Augusta.....	1	5	Lorain.....	0	1	1
Brunswick.....	1	1	Mansfield.....	0	1
Macon.....	1	1	Oklahoma:			
Rome.....	1	1	Oklahoma.....	1	4
Savannah.....	2	2	1	Tulsa.....	2	3
Valdosta.....	2	3	3	Pennsylvania:			
Illinois:				Allentown.....	0	1
Chicago.....	3	3	1	Chester.....	0	1
Indiana:				Lancaster.....	0	1
East Chicago.....	0	1	Philadelphia.....	10	3
Huntington.....	0	1	Pittsburgh.....	2	1
Iowa:				Scranton.....	0	1
Dubuque.....	0	1	Sharon.....	0	1
Kansas:				Swissvale.....	0	3
Kansas City.....	0	1	Washington.....	0	2
Wichita.....	0	2	1	South Carolina:			
Kentucky:				Charleston.....	4	2
Covington.....	1	1	Columbia.....	2	3	1
Louisville.....	5	3	Tennessee:			
Owensboro.....	1	1	Memphis.....	3	8
Maine:				Texas:			
Bangor.....	0	1	Dallas.....	4	3
Portland.....	0	1	El Paso.....	0	1	2
Maryland:				Fort Worth.....	1	2	1
Baltimore.....	7	2	2	Houston.....	1	1
Cumberland.....	0	1	San Antonio.....	1	1
Massachusetts:				Virginia:			
Boston.....	2	3	Danville.....	0	1
Chelsea.....	1	1	Richmond.....	1	1
Lynn.....	0	1	Roanoke.....	0	1
Pittsfield.....	0	1	Washington:			
Quincy.....	0	1	Spokane.....	0	1
Minnesota:				West Virginia:			
St. Paul.....	0	1	Charleston.....	3	1	1
Missouri:				Clarksburg.....	0	1
Joplin.....	0	1	Huntington.....	1	1
Kansas City.....	1	1	Wheeling.....	2	1
St. Louis.....	7	3	Wisconsin:			
New Jersey:				Manitowoc.....	0	1
Hackensack.....	0	1				
Morristown.....	1	1				
Newark.....	1	1	1				
Paterson.....	0	1				

CITY REPORTS FOR WEEK ENDED JULY 7, 1923—Continued.

DIPHTHERIA, MEASLES, SCARLET FEVER, AND TUBERCULOSIS.

City.	Popula- tion, Jan. 1, 1920.	Total deaths from all causes.	Diphtheria.		Measles.		Scarlet fever.		Tubercu- losis.	
			Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.
Alabama:										
Birmingham.....	178,806	52	3	1	38	2	1		10	6
Mobile.....	60,777	21	1						1	1
Montgomery.....	43,464	17			2					1
Tuscaloosa.....	11,906				7				3	
Arkansas:										
Fort Smith.....	28,870				4					
Little Rock.....	65,142				3					
California:										
Alameda.....	28,806	3			15					
Bakersfield.....	18,638	12	1							1
Eureka.....	12,923	4	1		20					
Glendale.....	13,536	6								
Long Beach.....	55,593	16	2		2				1	1
Los Angeles.....	576,673	174	43	2	74		30		45	24
Oakland.....	216,261	39	12	1	11	1	7			3
Pasadena.....	45,354	7			6		1		1	
Richmond.....	16,843	2								
Riverside.....	19,341	7					1			2
Sacramento.....	65,908	19	2		16	2	1		1	1
San Bernardino.....	18,721	12	1		2		3			2
San Diego.....	74,683	34	4		11		6		4	5
San Francisco.....	506,676	132	25	3	110		4		13	9
San Jose.....	39,642	11			8		2			
Santa Ana.....	15,485	9			7					
Santa Barbara.....	19,441	4								
Stockton.....	40,296	21	1		5		3			2
Colorado:										
Denver.....	256,491	53	36		35		9			7
Pueblo.....	43,050	12	1		3		1			1
Trinidad.....	10,906				1					
Connecticut:										
Bridgeport.....	143,555	18	6		2		3		4	3
Greenwich (town).....	22,123				2					
Hartford.....	138,036	24	2	1			1		3	2
Manchester (town).....	18,370	3	1							
Millford (town).....	10,193	1			3				1	
New Haven.....	162,537	35			4		4		2	4
New London.....	25,688	10	1		1					
Norwich (city).....	22,304	4	1				1			
Stonington (town).....	10,236	1			6					
Waterbury.....	91,715	23	4				5		3	
District of Columbia:										
Washington.....	437,571	102	2		27	1	6		25	9
Florida:										
Key West.....	18,749	6			2					
St. Petersburg.....	14,237	3								
Tampa.....	51,608	14			6		1			
Georgia:										
Albany.....	11,555				1					
Atlanta.....	200,616	81	1		10	2	2		5	4
Augusta.....	52,548	21	1		12	2				4
Brunswick.....	14,413	7								
Macon.....	52,995		1		4					
Rome.....	13,252		1		3					
Savannah.....	85,252	33	1		4				3	3
Valdosta.....	10,783	6								1
Idaho:										
Boise.....	21,393	7	1							
Illinois:										
Alton.....	24,682	2					1			
Aurora.....	36,397	13	1						4	
Bloomington.....	28,735	10			2					
Blue Island.....	11,424	6			5					
Chicago.....	2,701,705	505	61	4	139	7	55	1	161	48
Cicero.....	44,995	4							1	
Elgin.....	27,454	8			5					
Evanston.....	37,234				4					
Forest Park.....	10,768				4					
Freeport.....	19,669	3			10					
Galesburg.....	23,834	5							1	
Jacksonville.....	15,713	12								1
Kewanee.....	16,026	3								
La Salle.....	13,050	1								

CITY REPORTS FOR WEEK ENDED JULY 7, 1923—Continued.

DIPHTHERIA, MEASLES, SCARLET FEVER, AND TUBERCULOSIS—Continued.

City.	Popula- tion Jan. 1, 1920.	Total deaths from all causes.	Diphtheria.		Measles.		Scarlet fever.		Tuber- culosis.	
			Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.
Illinois—Continued.										
Mattoon.....	13,552	2
Oak Park.....	39,858	12	1	19
Quincy.....	35,978	10	2	8	2
Rock Island.....	35,177	2	14	2
Rockford.....	65,651	15	1	39	1	1
Springfield.....	50,183	18	1	16	1
Urbana.....	10,244	1	1
Indiana:										
Anderson.....	29,767	7	1	4	1
Bloomington.....	11,595	5
Crawfordsville.....	10,139	2	1
East Chicago.....	35,967	11	1	1
Elwood.....	10,790	7	1
Fort Wayne.....	86,549	27	12	3	1
Frankfort.....	11,585	2	3
Gary.....	55,378	6	2	1
Hammond.....	36,004	8	1	1	1
Huntington.....	14,000	3
Indianapolis.....	314,194	106	4	38	1	1	5	8
Kokomo.....	30,067	13	1	1
La Fayette.....	22,486	5	8	1
Logansport.....	21,626	2
Michigan City.....	19,457	11
Mishawaka.....	15,195	2
Muncie.....	36,524	11	23	4
Newcastle.....	14,458	1
South Bend.....	70,983	13	2	2	2	3	1
Terre Haute.....	66,083	14	4
Iowa:										
Burlington.....	24,057	7	1	3
Cedar Rapids.....	45,566	1
Clinton.....	24,151	0	1
Des Moines.....	126,468	1	6
Dubuque.....	39,141	1	2
Marshalltown.....	15,731	1
Muscatine.....	16,068	9	1
Sioux City.....	71,227	0	1	2
Waterloo.....	36,230	1	1
Kansas:										
Atchison.....	12,630	2	1
Coffeyville.....	13,452	6
Fort Scott.....	10,693	8
Kansas City.....	101,177	3	17	3
Lawrence.....	12,456	5	1	1
Parsons.....	16,028	1
Topeka.....	50,022	9	1	50
Wichita.....	72,217	21	15	1	1
Kentucky:										
Covington.....	57,121	10	2	1	2
Henderson.....	12,169	2
Lexington.....	41,534	13	1	4	1
Louisville.....	234,891	67	1	1	17	1
Owensboro.....	17,424	1	1
Paducah.....	24,735	1
Louisiana:										
New Orleans.....	387,219	112	5	36	19	12
Maine:										
Auburn.....	16,985	5	2
Bangor.....	25,978	7	2
Bath.....	14,731	2
Biddeford.....	18,008	2	1
Lewiston.....	31,791	7	21	1	1
Portland.....	69,272	27	1	1
Sanford (town).....	10,691	2
Maryland:										
Baltimore.....	733,826	181	19	81	1	35	1	31	20
Cumberland.....	29,837	7	1
Frederick.....	11,066	1	1	2
Massachusetts:										
Adams (town).....	12,967	2
Arlington (town).....	18,665	3	2
Attleboro.....	19,731	5
Belmont (town).....	10,749	3	11	1
Beverly.....	22,561	6

CITY REPORTS FOR WEEK ENDED JULY 7, 1923—Continued.

DIPHTHERIA, MEASLES, SCARLET FEVER, AND TUBERCULOSIS—Continued.

City.	Popula- tion Jan. 1, 1920.	Total deaths from all causes.	Diphtheria.		Measles.		Scarlet fever.		Tuber- culosis.	
			Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.
Massachusetts—Continued.										
Boston.....	748,060	146	45		68		32	2	35	18
Braintree (town).....	10,580	1			24					
Brockton.....	66,254	14	3		5		3		1	
Brookline.....	37,748	7			4		3			
Cambridge.....	109,694	24	3		3		8		2	2
Chelsea.....	43,184	7	2		2				1	1
Chicopee.....	36,214	3							2	1
Clinton.....	12,979	4								
Dedham.....	10,792	3								
Everett.....	40,120	3		1						
Fall River.....	120,485	23	2				1		3	1
Framingham.....	17,033	6					1		1	
Gardner.....	16,971	5			2					
Greenfield.....	15,462	3								1
Haverhill.....	53,884	4			21		7		1	
Holyoke.....	60,203	12	1		6		4			1
Lawrence.....	94,270	19	1		6		4			
Leominster.....	19,744	4			11				3	
Lowell.....	112,759	22	1		2		2		4	2
Lynn.....	99,148	18	2	1					1	1
Malden.....	49,103	8	1		3		4		1	
Medford.....	39,038	12	2		2				1	2
Melrose.....	18,204	5	1		12					
Methuen.....	15,189	6			4				1	
Natick.....	10,907		1				1		2	
New Bedford.....	121,217	19			1				5	1
Newburyport.....	15,618	6			2		1			
Newton.....	46,054	6			9		1		1	
North Adams.....	22,282	8			1					
Pesabody.....	19,552	2	1				1			
Pittsfield.....	41,763	11			1		2		5	1
Plymouth.....	13,045	2								
Quincy.....	47,876	11			4		4		1	
Somerville.....	93,091	17	3		3		2		2	1
Southbridge.....	14,245	2			4					
Springfield.....	129,614	20			1		2		5	1
Taunton.....	37,137	13	1				2			4
Wakefield.....	13,025	2			1		3		1	1
Watertown.....	21,457	5	2		7		1		2	
Westfield.....	18,604	2					1		1	
Winthrop.....	15,455	2					1		1	
Woburn.....	16,574	3								
Worcester.....	179,754	38	2	2			4		4	2
Michigan:										
Ann Arbor.....	19,516	12			9		1		1	
Battle Creek.....	36,164	0			33		1			
Benton Harbor.....	12,233	7			1		1			
Flint.....	91,599	18	3		26				7	
Grand Rapids.....	137,634	25	7		66		1		2	
Hamtramck.....	48,615	5	2							2
Highland Park.....	46,499	12	1		12		5		5	1
Holland.....	12,183						6			
Kalamazoo.....	48,487	13	1		29		2		1	1
Marquette.....	12,718	1	1		1		2			
Pontiac.....	34,273	6	4		11		9			
Port Huron.....	25,944	8			10		2	1		
Sault Ste. Marie.....	12,066	2			2					
Minnesota:										
Duluth.....	98,917	10			6		5		2	
Hibbing.....	15,089		1							
Mankato.....	12,469								1	
Minneapolis.....	380,582	71	11		11	2	25		18	7
Rochester.....	13,722	22			4					1
St. Paul.....	294,698	51	16		12		7		3	3
Winona.....	19,143	4			1		1			
Missouri:										
Cape Girardeau.....	10,252	2								
Joplin.....	29,902				1					
Kansas City.....	321,410	94	4	1	20	2	1		3	3
St. Joseph.....	77,939	27			11	1	1			
St. Louis.....	772,897	177	11		7		5		25	6
Springfield.....	39,631	16								

CITY REPORTS FOR WEEK ENDED JULY 7, 1923—Continued.

DIPHtheria, MEASLES, SCARLET FEVER, AND TUBERCULOSIS—Continued.

City.	Popula- tion Jan. 1, 1920.	Total deaths from all causes.	Diphtheria.		Measles.		Scarlet fever.		Tuber- culosis.	
			Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.
Montana:										
Billings.....	15,100	6					1		1	1
Great Falls.....	24,121	6	1		1					2
Helena.....	12,037	3			3					
Missoula.....	12,668	1					2			
Nebaska:										
Lincoln.....	54,948	15								
Omaha.....	191,601	52	2		2					4
Nevada:										
Reno.....	12,016	8					2		2	1
New Hampshire:										
Concord.....	22,167	6			8					1
Dover.....	13,029	3								
Keene.....	11,210	3			12					
Manchester.....	78,384	15	1	1	1	1				
New Jersey:										
Asbury Park.....	12,400	2			1					
Atlantic City.....	50,707	14			2					
Bayonne.....	76,754		3				1		1	
Belleville.....	15,660				2					
Bloomfield.....	22,019	2							1	
Clifton.....	26,470	2			1		1			
East Orange.....	50,710	9	1		7				5	
Elizabeth.....	95,783		3				2			
Garfield.....	19,381	1	1							
Hackensack.....	17,667	6			4		1		2	
Hoboken.....	68,166	12	1	1					1	2
Jersey City.....	298,103		6		5		1		2	
Kearny.....	26,724	3	4							1
Morristown.....	12,548	6								1
Newark.....	411,524	80	15	2	36		8		21	5
Orange.....	33,268	5			1		1			
Passaic.....	63,841	10	2		3				3	1
Paterson.....	135,875		8		52		1		5	
Perth Amboy.....	41,707	6			1		1		3	
Phillipsburg.....	16,923	3								
Plainfield.....	27,700	6			1		1			
Summit.....	10,174	1			4					
Trenton.....	119,289	27	8	1			1		5	
Union (town).....	20,651				1					
West Hoboken.....	40,074	3							1	
West New York.....	29,926	3							1	
West Orange.....	15,573	1			3		1		1	
New York:										
Albany.....	113,344		1		44		2		4	
Amsterdam.....	33,524	5			14					
Auburn.....	36,192	8	1						2	1
Buffalo.....	505,775	101	10	3	42	1	9		17	12
Cohoes.....	22,987	2			3				2	
Hornell.....	15,025	2			11		2			
Hudson.....	11,745	3			4				1	
Ithaca.....	17,001	3			4				2	
Lackawanna.....	17,918	2	1		18				1	
Little Falls.....	13,029	9								
Lockport.....	21,308	8			1				1	
Middletown.....	18,420				1				1	
Mount Vernon.....	42,726	12	1				1		1	
New York.....	5,620,018	1,010	128	7	207	2	50		1224	191
Newburgh.....	30,366	5	1						3	
Niagara Falls.....	50,760	10	3		7				5	
North Tonawanda.....	15,482	4			28		2	1		1
Ogdensburg.....	14,609	5								
Olean.....	20,503	9			4		8			
Peekskill.....	15,858	3			3		2		2	
Plattsburg.....	10,909	3								
Poughkeepsie.....	35,000	9			4				3	
Rochester.....	295,750	50	4	2	23		3			
Rome.....	26,341	4		1	1					
Saratoga Springs.....	13,181	5			1		4		1	1
Schenectady.....	88,723	18	2		78		1		6	3
Syracuse.....	171,717	46	8		91	4	5		4	3
Troy.....	72,013	24			7		1		2	2
Watertown.....	31,285	9			22					
Yonkers.....	100,176	13	6		7		2			4

¹ Pulmonary only.

CITY REPORTS FOR WEEK ENDED JULY 7, 1923—Continued.

DIPHTHERIA, MEASLES, SCARLET FEVER, AND TUBERCULOSIS—Continued.

City.	Popula- tion Jan. 1, 1920.	Total deaths from all causes.	Diphtheria.		Measles.		Scarlet fever.		Tuber- culosis.	
			Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.
North Carolina:										
Durham.....	21,719	6								
Greensboro.....	43,525	8			14					1
Raleigh.....	24,418	10			3					
Rocky Mount.....	12,742	5								1
Salisbury.....	13,884	5								
Wilmington.....	33,372	9								1
Winston-Salem.....	48,395	22			81	1	2		3	4
North Dakota:										
Fargo.....	21,931	0	2							
Ohio:										
Akron.....	208,435	32	3		8		3		10	
Ashtabula.....	22,082	7	1			1				1
Barberton.....	18,811	3								
Bucyrus.....	10,425	1					1			
Cambridge.....	13,104	3	1						1	
Chillicothe.....	15,831	4								
Cincinnati.....	401,247	111	5		44		3		10	10
Cleveland.....	793,811	157	22		67		33	1	25	11
Cleveland Heights.....	15,236	1			2					
Columbus.....	237,031	52	5		2		2		7	4
Coshocton.....	10,847	1								
Dayton.....	152,559	34	1		2		2		1	
East Cleveland.....	27,292	4			1		3			1
East Youngstown.....	17,237	4				2				
Findlay.....	17,021	7								
Fremont.....	12,468						1			
Lancaster.....	14,706	4								
Lima.....	41,326	10	1		3				2	
Lorain.....	37,295		1		2		3			
Mansfield.....	27,824	5			3					
Martins Ferry.....	11,634	4								
Middletown.....	23,594	4	1							
New Philadelphia.....	10,718				5		1			
Newark.....	20,718	10			6					
Niles.....	13,080	4			2		1		1	1
Norwood.....	14,966				1		1			
Piqua.....	15,044	4								
Salem.....	10,305	0	1		11					
Sandusky.....	22,897	3					1			
Springfield.....	60,840	18			2				1	2
Steubenville.....	28,508	8			1		1			
Tiffin.....	14,375	3			1					
Toledo.....	243,164	53	2		16		21		3	6
Youngstown.....	132,358	31	5	3	21	1	2			2
Zanesville.....	29,569	9					1		1	
Oklahoma:										
Oklahoma.....	91,295	19			6		2			
Oregon:										
Portland.....	258,288	57	6				2		6	4
Pennsylvania:										
Allentown.....	73,502				2				5	
Altoona.....	60,331				2					
Ambridge.....	12,730				3		1			
Berwick.....	12,181		1							
Bethlehem.....	50,358		3		7		1			
Bradford.....	15,525				1					
Bristol.....	10,273		1		1					
Canonsburg.....	10,632						1			
Carbondale.....	18,640		1		1					
Chester.....	58,030		3		2				6	
Donora.....	14,131				1					
Dubois.....	13,681									
Erie.....	93,372		3		23				1	
Farrell.....	15,586		1				2			
Greensburg.....	15,033						1			
Harrisburg.....	75,917		1							
Hazleton.....	32,277				2					
Homestead.....	20,452				4					
Jeannette.....	10,627		1							
Johnstown.....	67,327		1				2		6	
Lancaster.....	53,150		1		7					
Lebanon.....	24,643		9		1		5			
McKees Rocks.....	16,713		1						1	

CITY REPORTS FOR WEEK ENDED JULY 7, 1923—Continued.

DIPHTHERIA, MEASLES, SCARLET FEVER, AND TUBERCULOSIS—Continued.

City.	Popula- tion Jan. 1, 1920.	Total deaths from all causes.	Diphtheria.		Measles.		Scarlet fever.		Tuber- culosis.	
			Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.
Pennsylvania—Continued.										
McKeesport.....	46,781		2		1					
Meadville.....	14,568				4					
Monessen.....	18,179		1							
Norristown.....	32,319				2		2			
North Braddock.....	14,928				2		2			
Oil City.....	21,274				1					
Olyphant.....	10,236		1							
Philadelphia.....	1,823,779	329	27	1	12		23	2	77	25
Pittsburgh.....	583,343	125	16	1	16	1	7	3		5
Reading.....	167,781		1							
Scranton.....	137,783		1		7		1			
Steelton.....	13,428		1							
Swissvale.....	10,908		1							
Tamaqua.....	12,363		1		3					
Warren.....	14,272				2					
Washington.....	21,480				19					
Wilkes-Barre.....	73,833		1		29		1		2	
Wilkesburg.....	24,403		3		3					
Williamsport.....	36,198						4			
Woodlawn.....	12,495				1				1	
York.....	47,512				4		1			
Rhode Island:										
Cranston.....	29,467	8								
Cumberland (town).....	10,677	3								
Newport.....	30,255	6	1	1						
Pawtucket.....	64,248	11	3							
Providence.....	237,595	53	3		4		3			2
Woonsocket.....	43,496	5								
South Carolina:										
Charleston.....	67,957	30			12	1				4
Columbia.....	37,524	27			2					2
Greenville.....	23,127	0	1				1			
South Dakota:										
Sioux Falls.....	25,202	4								
Tennessee:										
Knoxville.....	77,818		1		3				1	1
Memphis.....	162,351	78			2		2		20	5
Nashville.....	118,342	48	1						3	3
Texas:										
Amarillo.....	15,491	6			1				1	1
Beaumont.....	40,422	6	1				1		3	2
Dallas.....	158,976	36	4		11		3		6	5
El Paso.....	77,569	33			2		3		1	1
Fort Worth.....	106,482	14	3		3		1		1	1
Galveston.....	44,255	8			2					3
Houston.....	138,276	45								5
San Antonio.....	161,379	48	1		5				9	5
Waco.....	38,500	5	1							
Utah:										
Provo.....	10,303	6								
Salt Lake City.....	118,110	20	3		10		1			2
Vermont:										
Burlington.....	22,779	9	1		4		1			
Virginia:										
Alexandria.....	18,060	8			2					
Charlottesville.....	10,688	9								1
Danville.....	21,539	7			4					
Lynchburg.....	30,670	10			2		1		1	1
Norfolk.....	115,777				31				6	3
Petersburg.....	31,012	9							2	
Richmond.....	171,667	57			69				3	5
Roanoke.....	50,842	13			2				1	
Washington:										
Bellingham.....	25,585				1					
Seattle.....	315,312		3		44		4			
Spokane.....	104,437		1		5		2			
Tacoma.....	96,965		4		3		6		11	
Yakima.....	18,539				1					
West Virginia:										
Bluefield.....	15,282	8	1							1
Charleston.....	39,608	6	1		1		1			
Clarksburg.....	27,869	4			16		1			
Fairmont.....	17,851				1				2	

DIPHTHERIA, MEASLES, SCARLET FEVER, AND TUBERCULOSIS—Continued.

City.	Population Jan. 1, 1920.	Total deaths from all causes.	Diphtheria.		Measles.		Scarlet fever.		Tuberculosis.	
			Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.	Cases.	Deaths.
West Virginia—Continued.										
Huntington.....	50,177	29			1				5	1
Martinsburg.....	12,515		1		1					
Parkersburg.....	20,050	5							1	1
Wheeling.....	56,248	12	1		2		4		1	
Wisconsin:										
Appleton.....	19,561	2	1		4				1	
Ashland.....	11,334	1			5		5			
Beloit.....	21,284	3			1		6			
Eau Claire.....	20,906				22					
Fond du Lac.....	23,427	6					1			
Green Bay.....	31,017				2		5			
Janesville.....	18,293	2			1		1			
Kenosha.....	40,472	4	3						4	1
La Crosse.....	30,421				2		1		8	
Madison.....	38,378	3	1		10					
Manitowish.....	17,563		1		6					
Marinette.....	13,610		1		12				1	
Milwaukee.....	457,147	62	13	2	16		29		14	4
Oshkosh.....	33,162	6			2	1				1
Racine.....	58,593	7	1				3			
Sheboygan.....	30,955	5	1						3	
Superior.....	39,671	8	1		3		2			
Waukesha.....	12,558				6					
Wausau.....	18,661				2		2			
West Allis.....	13,745		1		2					

FOREIGN AND INSULAR.

BRAZIL.

Yellow Fever—Bahia.

During the week ended June 9, 1923, a case of yellow fever was reported at Bahia, Brazil.

CANADA.

Communicable Diseases—Ontario—June, 1923.

Communicable diseases were notified in the Province of Ontario, Canada, during the month of June, 1923, as follows:

Disease.	June, 1923.		June, 1922.	
	Cases.	Deaths.	Cases.	Deaths.
Cerebrospinal meningitis.....	3	3	3	3
Chancroid.....	1			
Diphtheria.....	203	22	191	19
Gonorrhea.....	174		210	
Influenza.....		13		
Lethargic encephalitis.....	7	6		
Measles.....	2,149	14	2,163	4
Pneumonia, primary.....		150		140
Pneumonia, influenzal.....				18
Scarlet fever.....	228	20	151	5
Smallpox.....	13		104	
Syphilis.....	166		219	
Tuberculosis.....	188	147	204	141
Typhoid fever.....	38	11	24	2
Whooping cough.....	199	19	65	6

CUBA.

Communicable Diseases—Habana.

Communicable diseases have been notified at Habana as follows:

Disease.	July 1-10, 1923.		Cases remaining under treatment July 10, 1923.
	New cases.	Deaths.	
Chicken pox.....			5
Diphtheria.....	2	1	2
Leprosy.....	1		13
Malaria.....	52		52
Measles.....	2		10
Paratyphoid fever.....	1		5
Scarlet fever.....			3
Typhoid fever.....	14	44	44

¹ From abroad, 1.

² From the interior, 25.

³ From the interior, 27.

FRANCE.**Typhus Fever—Marseille.**

During the three months ended June 30, 1923, three fatal cases of typhus fever were reported at Marseille, France.

GREAT BRITAIN.**Health Conditions—London—Comparative.**

Information has been received under date of June 18, 1923, showing that from December 23, 1922, to May 26, 1923, the death rate (annual basis) of London was 12.5 as compared with 13 for 105 great towns in England during the same period.

Smallpox—Gloucestershire.

Information received under date of June 28, 1923, shows the presence of smallpox in mild form, with no fatalities, in Gloucestershire, England. A few cases were reported in the city of Bristol. These cases were stated to be similar in every respect to the cases observed at Bristol during 1903 and 1904. In the city of Gloucester (population, about 50,000) 123 cases were reported present in one hospital; cases were also reported in the rural districts.

JAMAICA.**Smallpox (Reported as Alastrim).**

During the two weeks ended June 23, 1923, 83 cases of smallpox (reported as alastrim) were notified in the Island of Jamaica. Of these, 17 cases occurred in the Parish of Kingston.

Typhoid Fever—Vicinity of Kingston.

During the same period, 31 cases of typhoid fever were reported in the vicinity of Kingston.

LATVIA.**Communicable Diseases—April, 1923.**

Communicable diseases were reported in the Republic of Latvia, during the month of April, 1923, as follows:

Disease.	Cases.	Disease.	Cases.
Diphtheria.....	71	Typhoid fever.....	78
Measles.....	49	Typhus fever.....	96
Scarlet fever.....	158	Whooping cough.....	38
Smallpox.....	3		

Other Diseases—April, 1923.

During the month of April, 1923, other diseases were reported in the Republic of Latvia as follows: Anthrax, 1 case; dysentery, 5 cases; leprosy, 3; malaria, 3.

MADAGASCAR.**Plague.**

During the period May 1 to 15, 1923, 15 cases of plague with 15 deaths were reported in the island of Madagascar, occurring in the Province of Tananarive. For distribution according to locality of occurrence and type of disease see p. 1741.

Rats Killed—Tananarive.

During the month of March, 1923, 1,829 rats were killed in the suburban district of Tananarive.

MALTA.**Public Health Conditions—Year 1921-22.**

The report of the minister for public health of the island of Malta for the year 1921-22, received under date of May 17, 1923, shows that mortality for all ages was practically within the levels reached in previous years. Infant mortality remained high in some districts but showed improvement in others. The absence of dangerous contagious diseases, notably cholera, plague, and smallpox, which were present in countries surrounding Malta, was noted. Typhoid fever and undulant fever were stated not to have abated, but the proportion of fatalities to cases of these diseases was stated to be the lowest on record. The improvement in health conditions, expressed in terms of diminution of sickness, better health conditions, and increased length of life were attributed to the spread of education, confidence in the measures of disease prevention, and improved economic conditions.

The government health service maintains, in addition to general hospitals, a hospital for incurables, leper hospital, hospital for the insane, orphan asylums, and 30 government dispensaries, and also provides gratuitous care in maternity cases.

MAURITIUS.**Plague.**

Information received under date of May 25, 1923, shows the occurrence of a case of plague at Port Louis, Mauritius, May 4, 1923, and of the further occurrence in the island of one case reported May 21, 1923.

CHOLERA, PLAGUE, SMALLPOX, TYPHUS FEVER, AND YELLOW FEVER.

The reports contained in the following tables must not be considered as complete or final as regards either the list of countries included or the figures for the particular countries for which reports are given.

Reports Received During Week Ended July 27, 1923.¹**CHOLERA.**

Place.	Date.	Cases.	Deaths.	Remarks.
India:				
Bombay.....	June 3-9.....	8	3	
Madras.....	do.....	1		

PLAGUE.

Ceylon:				
Colombo.....	May 27-June 2.....	1	2	From outside city.
China:				
Amoy.....	May 27-June 9.....		3	
Foochow.....	May 27-June 16.....			Present in endemic form.
India:				
Bombay.....	May 20-June 9.....	107	95	Apr. 22-28, 1923: Cases, 111; deaths, 84.
Karachi.....	June 3-9.....	11	8	
Madras Presidency.....	do.....	20	10	
Java:				
East Java—				
Soerabaya.....	May 13-19.....	1	1	
Madagascar:				
Province—				
Tananarive.....	May 1-15.....	9	9	May 1-15, 1923: Cases, 15; deaths, 15.
Tananarive.....	do.....	6	6	Bubonic and septicemic. Septicemic.
Mauritius (Island):				
Port Louis.....	May 4.....	1		May 4-21, 1923: Two cases.

SMALLPOX.

Brazil:				
Pernambuco.....	May 27-June 2.....	2		
Canada:				
Manitoba—				
Winnipeg.....	June 3-30.....	4		
New Brunswick—				
Kent County.....	July 1-7.....	1		
Ontario.....				June 1-30, 1923: Cases, 13.
Toronto.....	June 24-30.....	3		
Saskatchewan—				
Regina.....	do.....	1		
Ceylon:				
Colombo.....	May 27-June 2.....		1	Outside city.
China:				
Amoy.....	May 27-June 9.....			Present.
Foochow.....	May 27-June 16.....			Do.
Egypt:				
Cairo.....	Mar. 12-25.....	2	1	
Great Britain:				
Birmingham.....	June 18-30.....	3		
Bristol.....	June 28.....			Present.
Cardiff.....	June 24-30.....	1		
Gloucester.....	June 28.....			123 cases reported in hospital; present in rural districts.
India:				
Bombay.....	Apr. 22-June 9.....	136	64	
Karachi.....	June 3-9.....	2	1	
Madras.....	do.....	6		
Jamaica.....				June 10-23, 1923: Cases, 83. (Reported as alastrim.)
Kingston.....	June 10-23.....	17		In parish.
Java:				
East Java—				
Soerabaya.....	May 13-26.....	27	7	
Latvia.....				Apr. 1-30, 1923: Cases, 3.
Mexico:				
Mexico City.....	June 3-9.....	42		Including municipalities in Federal District.

¹ From medical officers of the Public Health Service, American consuls, and other sources.

CHOLERA, PLAGUE, SMALLPOX, TYPHUS FEVER, AND YELLOW FEVER—Continued.

Reports Received During Week Ended July 27, 1923—Continued.

SMALLPOX—Continued.

Place.	Date.	Cases.	Deaths.	Remarks.
Portugal:				
Lisbon.....	June 4-16.....	3	1	
Oporto.....	June 24-30.....	2		
Spain:				
Valencia.....	June 17-23.....	15	1	
Switzerland:				
Basel.....	June 10-16.....	1		
Berne.....do.....	4		
Syria:				
Damascus.....	June 5-11.....	5		
Tunis:				
Bizerta.....	June 10-20.....	1		
Union of South Africa:				
Cape Province.....	May 26-June 2.....			Outbreaks.
Transvaal.....do.....			Do.
Yugoslavia:				
Serbia—				
Belgrade.....	June 10-16.....	1	1	

TYPHUS FEVER.

China:				
Antung.....	May 28-June 10...	9		
Egypt:				
Alexandria.....	June 11-17.....	4	1	
Cairo.....	Mar. 12-Apr. 1....	9	8	
France:				
Marseille.....	Mar. 1-May 31....		3	
Germany:				
Stettin.....	June 3-9.....	1		
Latvia.....				Apr. 1-30, 1923: Cases, 96.
Mexico:				
Mexico City.....	June 3-19.....	17		Including municipalities in Federal District.
Rumania:				
Kishineff.....	May 1-31.....	28		
Tunis:				
Tunis.....	June 18-24.....		1	
Union of South Africa:				
Cape Province.....	May 20-June 9....			Outbreaks.
Orange Free State.....	May 20-26.....			Do.
Yugoslavia:				
Croatia—				
Zagreb.....	May 27-June 2....	1		

YELLOW FEVER.

Brazil:				
Bahia.....	June 3-9.....	1		

CHOLERA, PLAGUE, SMALLPOX, TYPHUS FEVER, AND YELLOW FEVER—Continued.

Reports Received from June 30 to July 20, 1923.¹

CHOLERA.

Place.	Date.	Cases.	Deaths.	Remarks.
India.....				Apr. 15-June 2, 1923: Cases, 9, 250; deaths, 8, 126.
Calcutta.....	May 6-June 2.....	206	171	
Rangoon.....	May 13-26.....	7	6	
Philippine Islands:				
Province—				
Laguna.....	June 3-9.....	1		
Mountain.....	Mar. 25-31.....	1	1	
Siam:				
Bangkok.....	May 13-19.....	3	4	

PLAGUE.

Australia:				
Sydney.....	June 30.....	1	1	
Azores:				
St. Michael Island.....	May 6-26.....	12	5	In one locality.
British East Africa:				
Kenya—				
Tanganyika.....	May 6-12.....	1	1	
Canary Islands:				
Las Palmas.....	June 7.....	1		
Ceylon:				
Colombo.....	May 6-26.....	7	10	Plague rats, 32.
China:				
Amoy.....	May 13-26.....		3	
Hongkong.....	Apr. 29-May 26.....	29	14	
Ecuador:				
Guayaquil.....				May 16-31, 1923: Rats examined, 4,800; found infected, 21.
Hawaii:				
Hamakua.....				Plague-infected rats: Pohakea, May 23, 1923, 1 rat; vicinity of Pacific Sugar Co. mill, June 2, 1 rat.
India:				
Bombay.....	Apr. 29-May 19.....	261	214	
Calcutta.....	May 6-June 2.....	13	12	
Karachi.....	May 13-June 2.....	81	61	
Madras Presidency.....	May 13-June 2.....	230	128	
Rangoon.....	May 6-26.....	85	76	
Java:				
East Java—				
Soerabaya.....	Apr. 1-30.....	487	487	May 16, 1923: Epidemic in five districts.
Soerakarta.....				
Madagascar:				
Province—				
Tananarive.....	Apr. 1-30.....	39	36	Apr. 1-30, 1923: Cases, 51; deaths, 48. Bubonic, pneumonic, septicemic.
Tananarive.....	Apr. 16-30.....	12	12	
Mexico:				
Tampico.....				Apr. 15-21, 1923: 1 plague rat.
Peru:				
Locality—				May 1-31, 1923: Cases, 57; deaths, 27.
Ayabaca.....	May 16-31.....	2		
Callao.....	May 1-31.....	3	1	
Canete.....	May 16-31.....	2	2	
Cerro Azul.....	May 1-31.....	3	1	
Chiclayo.....	do.....	8	2	
Cutervo.....	May 1-15.....	2	1	
Huancabamba.....	May 1-31.....	18	13	
Lima (city).....	do.....	5	1	
Lima (country).....	do.....	5	3	
Salaverry.....	do.....	7	2	
Trujillo.....	do.....	2	1	
Siam:				
Bangkok.....	Apr. 29-May 26.....	16	14	
Straits Settlements:				
Singapore.....	May 6-12.....		2	

¹ From medical officers of the Public Health Service, American consuls, and other sources. For reports received from Dec. 30, 1922, to June 29, 1923, see Public Health Reports for June 29, 1923. The tables of epidemic diseases are terminated semiannually and new tables begun.

CHOLERA, PLAGUE, SMALLPOX, TYPHUS FEVER, AND YELLOW FEVER—Continued.

Reports Received from June 30 to July 20, 1923—Continued.

SMALLPOX.

Place.	Date.	Cases.	Deaths.	Remarks.
Algeria:				
Algiers.....	May 1-31.....	2		
Arabia:				
Aden.....	May 27-June 2.....		1	
Bolivia:				
La Paz.....	Apr. 1-30.....	1	2	
Brazil:				
Pernambuco.....	May 6-19.....	3		
Rio de Janeiro.....	May 13-26.....	4	1	
British East Africa:				
Kenya—				
Mombasa.....	May 20-26.....	1		From vessel from Bombay.
Tanganyika.....	Apr. 29-May 5.....	2		
Canada:				
Alberta—				
Calgary.....	May 27-June 2.....	1		Infection from Deer Lodge, Mont.
British Columbia—				
Vancouver.....	May 27-June 23.....	31		
Quebec—				
Quebec.....	June 10-16.....	1		Varioloid.
Ceylon:				
Colombo.....	May 6-19.....	23		
Chile:				
Concepcion.....	May 22-28.....		2	
Valparaiso.....	May 7-June 2.....		107	
China:				
Amoy.....	May 13-26.....		2	
Antung.....	May 14-20.....	1		
Chungking.....	May 13-June 2.....			Present.
Foochow.....	May 13-26.....			Do.
Hongkong.....	Apr. 29-May 26.....	33	31	
Manchuria—				
Dairen.....	May 21-27.....	1		
Harbin.....	May 7-27.....	2		
Mukden.....	May 13-20.....	1		
Nanking.....	May 13-26.....			Do.
Shanghai.....	May 21-June 3.....	4		Foreign.
Chosen (Korea):				
Chemulpo.....	May 1-31.....	1		
Fusan.....	do.....	1		
Gensan.....	do.....	1		
Seoul.....	do.....	33	9	
Czechoslovakia:				
Ecuador:				
Guayaquil.....	May 16-31.....	1		Jan.-Mar., 1923: Cases, 15.
Finland:				
Great Britain:				
Cardiff.....	June 3-9.....	5		May 1-15, 1923: 1 case.
Greece:				
Patras.....	Apr. 24-May 13.....		11	
Saloniki.....	Apr. 30-May 20.....	2	2	
India:				
Bombay.....	Apr. 29-May 19.....	110	50	Apr. 15-May 5, 1923: Cases, 4,973; deaths, 1,424.
Calcutta.....	May 13-26.....	5	4	
Karachi.....	May 13-June 2.....	18	6	
Madras.....	do.....	17	3	
Rangoon.....	May 6-26.....	80	32	
Iraq (Mesopotamia):				
Bagdad.....	Apr. 1-30.....	10		
Italy:				
Turin.....	May 28-June 3.....	1		
Jamaica:				
Kingston.....	May 27-June 9.....	17		May 27-June 9, 1923: Cases, 124 (reported as alastrim).
Japan:				
Kobe.....	May 28-June 10.....	2		
Javn:				
East Java—				
Soerabaya.....	Apr. 22-May 12.....	72	10	
West Java—				
Batavia.....	May 5-25.....	9	2	Province.
Mexico:				
Chihuahua.....	June 11-24.....	7		
Mexico City.....	May 19-26.....	36		Including municipalities in Federal District.
Palestine:				
Jaffa.....	June 5-11.....	1		

CHOLERA, PLAGUE, SMALLPOX, TYPHUS FEVER, AND YELLOW FEVER—Continued.

Reports Received from June 30 to July 29, 1923—Continued.

SMALLPOX—Continued.

Place.	Date.	Cases.	Deaths.	Remarks.
Persia:				
Tabriz.....	Apr. 1-14.....		1	District.
Portugal:				
Lisbon.....	May 20-June 2.....	20		May 28-June 9, 1923: Cases, 8; deaths, 2.
Oporto.....	June 10-19.....	4	3	
Portuguese West Africa:				
Angola—				
Loanda.....	Apr. 1-21.....		2	
Rhodesia (British Africa):				
Northern Rhodesia.....	May 8-14.....	21	8	
Southern Rhodesia.....	May 3-16.....	4	2	
Siam:				
Bangkok.....	Apr. 29-May 19.....	43	16	
Sierra Leone:				
Kaballa.....	May 1-15.....	1		In Sembahun district.
Pujehun.....	May 16-31.....	1		
Spain:				
Barcelona.....	May 31-June 6.....		1	
Valencia.....	May 15-June 16.....	25	1	
Switzerland:				
Basel.....	May 27-June 9.....	2		
Berne.....	May 20-29.....	6		
Lucerne.....	May 1-31.....	29		
Zurich.....	May 20-June 2.....	6		
Syria:				
Damascus.....	May 15-21.....	2		
Tunis:				
Tunis.....	June 11-17.....	1		
Turkey:				
Constantinople.....	May 13-29.....		29	
Union of South Africa:				
Cape Province.....	May 6-12.....			Outbreaks.
Orange Free State.....	Apr. 29-May 14.....			Do.
On vessel:				
S. S. Kargala.....	May 20-26.....	1		At Mombasa, British East Africa; vessel arrived from Bombay, Mar. 25, 1923. Two cases, in quarantine (reported as alastrim). Vessel left Victoria, B. C., Apr. 28, 1923. Touched at Honolulu.
S. S. Makura.....	May 26.....	2		

TYPHUS FEVER.

Algeria:				
Algiers.....	May 1-31.....	41	14	
Chile:				
Concepcion.....	May 22-June 4.....		2	
Talcahuano.....	May 12-19.....	1		
Valparaiso.....	May 7-June 2.....		13	
China:				
Hankow.....	May 19-25.....	1		
Manchuria—				
Harbin.....	May 6-13.....	1		
Mukden.....	May 14-20.....	2		
Czechoslovakia.....				Jan.-Mar., 1923: Cases, 191; deaths, 6.
Egypt:				
Alexandria.....	May 14-June 10.....	3	3	
Germany:				
Coblenz.....	May 27-June 2.....		1	
Hamburg.....	May 20-26.....	3		
Kölnesberg.....	May 12-June 2.....	2		
Stettin.....	May 27-June 2.....		1	
Greece:				
Patras.....	Apr. 24-May 13.....		18	
Saloniki.....	Apr. 30-May 27.....	27	4	Recurrent typhus: Cases, 3; deaths, 3.
Guatemala:				
Guatemala City.....	Apr. 1-May 31.....		4	
Hungary:				
Budapest.....	Jan. 1-June 2.....	48	12	Jan. 1-May 19, 1923: Cases, 318; deaths, 36. In 11 counties.
Iraq (Mesopotamia):				
Bagdad.....	Apr. 1-50.....	2		

CHOLERA, PLAGUE, SMALLPOX, TYPHUS FEVER, AND YELLOW FEVER—Continued.

Reports Received from June 30 to July 20, 1923—Continued.

TYPHUS FEVER—Continued.

Place.	Date.	Cases.	Deaths.	Remarks.
Mexico:				
Mexico City.....	May 20-26.....	15		Including municipalities in Federal district.
Palestine:				
Jaffa.....	May 22-28.....	2		
Jerusalem.....	do.....	1		
Persia:				
Tabriz.....	Apr. 1-14.....	2		
Poland.....				Mar. 4-Apr. 7, 1923: Cases, 2,253; deaths, 172. Recurrent typhus: Cases, 338; deaths, 6.
Portugal:				
Oporto.....	June 10-16.....	1		
Russia (Soviet).....				Feb. 1-28, 1923: Cases, 17,577. Recurrent, Jan. 1-Feb. 28, 1923: Cases, 43,540.
Spain:				
Madrid.....	May 1-31.....		1	
Syria:				
Aleppo.....	May 20-26.....	3	1	
Beirut.....	May 1-10.....	1		
Tunis:				
Tunis.....	May 28-June 17...	3	1	
Turkey:				
Constantinople.....	May 13-26.....		13	
Union of South Africa:				
Cape Province.....	Apr. 20-May 12...			Outbreaks.
Orange Free State.....	May 6-12.....			Do.
Transvaal.....	do.....			Do.

YELLOW FEVER.

Brazil:				
Bahia.....	May 13-June 2....	16	5	